1998

Advances in the Chemistry of Fullerene Fragments.

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ADVANCES IN THE CHEMISTRY OF FULLERENE FRAGMENTS

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
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in partial fulfillment of the
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Doctor of Philosophy

in

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by
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B. S. University of Kentucky, May 1994
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TABLE OF CONTENTS

ABSTRACT

This dissertation deals with the synthesis and characterization of novel intermediate target molecules that when placed under pyrolytic conditions, yield polynuclear aromatic hydrocarbons that can be identified on the surface of buckminsterfullerene. It also presents some direct applications that have developed from some significant synthetic improvements of key intermediates required for production of novel fullerene fragments.

Chapter one presents the synthetic routes used to prepare $C_{32}H_{12}$ and attempts toward synthesizing $C_{40}H_{14}$ and $C_{46}H_{20}$. The novel $C_{32}H_{12}$ is only the second known fullerene fragment that contains more than thirty carbon atoms. It is successfully produced by flash vacuum pyrolysis by either 7,10-bis(2-bromophenyl)benzo[*k*]-fluoranthene or 7,10-bis(2,5-dibromophenyl)benzo[*k*]-fluoranthene.

Chapter two outlines a significant improvement in the production of 1,2,5,6-tetraketopyracene, a key intermediate in the synthesis of $C_{30}H_{12}$. An unreliable and low yield three step synthesis is replaced by a one step high yield conversion of 1,2-diketopyracene to 1,2,5,6-tetraketopyracene via oxidation with benzeneseleninic anhydride. In addition, chapter two discusses an extension of this methodology to include oxidation of benzylic alkenes. This represents a new and unprecedented synthetic transformation of benzylic alkenes to 1,2-diketones.

CHAPTER 1: SYNTHESIS OF NOVEL FULLERENE FRAGMENTS

1.1 Introduction

In 1985 the discovery of C_{60}, commonly referred to as buckyball, by Kroto, Heath, O'Brien, Curl, and Smalley[1.1] ignited an overwhelming amount of research activity. In addition to diamond and graphite, this discovery represented a new allotrope of carbon. Its structure is exactly that of the European football or the American soccer ball consisting of 20 hexagons and 12 pentagons.(**Figure 1.1.1**)

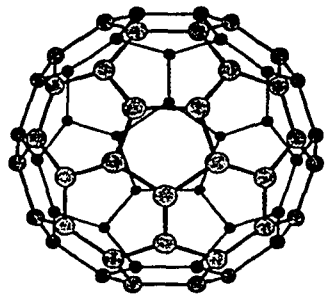


Figure 1.1.1

When dissected it consists of upper and lower C_{20} polar caps connected by a C_{20} belt.(**Figure 1.1.2**) It was given the common name Buckminsterfullerene in tribute to the late Buckminster Fuller for his work on geodesic domes. This common name came to be a necessity as its proper IUPAC name is given below:

Hentriacontacyclo[29.29.0.0.^{2,14}.0^{3,12}.0^{4,59}.0^{5,10}.0^{6,58}.0^{7,55}.0^{8,53}.0^{9,21}.0^{11,20}.0^{13,18}.0^{15,30}.0^{16,28}.0^{17,25}.0^{19,24}.0^{22,52}.0^{23,50}.0^{26,49}.0^{27,47}.0^{29,45}.0^{32,44}.0^{33,60}.0^{34,57}.0^{35,43}.0^{36,56}.0^{37,41}.0^{38,54}.0^{39,51}.0^{40,48}.0^{42,46}]hexaconta-1,3,5(10),6,8,11,13(18),14,16,19,21,23,25,27,29(45),30,32(44),33,35,(43)36,38,(54),39(51),40(48),41,46,49,52,55,57,59-triacontaene.

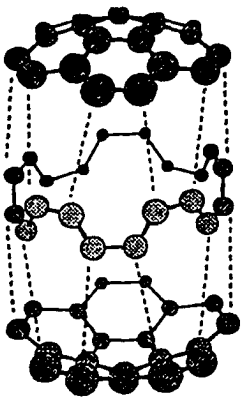
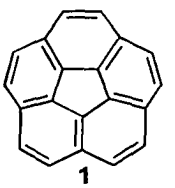


Figure 1.1.2

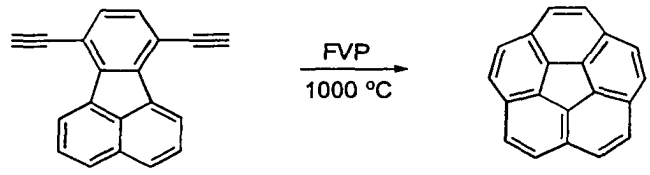
This truly remarkable and unprecedented result also reestablished the significance of Barth and Lawton's 1967 landmark synthesis of corannulene[1.2] (**1**), as it is represented on the surface of C_{60} and thus is considered to be the first curved fullerene fragment.



1

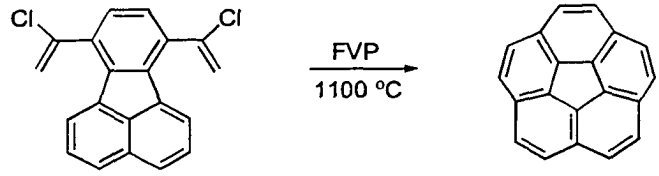
Given that C_{60} is made up of two corannulenes connected by a C_{20} belt it is obvious why synthetic chemists have sought to improve and expand upon the synthetic methodology which led to the creation of corannulene. The first step toward improving Barth's synthesis was made by Scott in 1991 when 7, 10-diethynylfluoranthene (**Scheme 1.1.1**) was subjected to flash vacuum pyrolysis at 1000 °C to produce corannulene as a sole product.[1.3]

Although the yield (10%) was not sufficient to use this system as a preparative method, it was significant in showing that flash vacuum pyrolysis was a



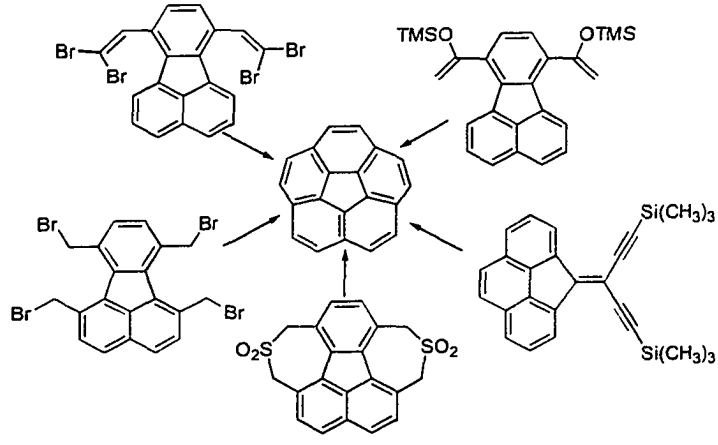
Scheme 1.1.1

possible technique for producing corannulene. It was only one year later when Scott and coworkers employed the same technique to 7,10-dichlorovinyl-fluoranthene (**Scheme 1.1.2**) to produce corannulene in 35-40% yield.[1.4]



Scheme 1.1.2

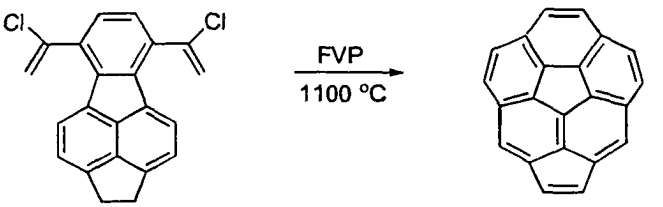
This improvement in yield was sufficient to allow the production of corannulene in gram scale quantities.



Scheme 1.1.3

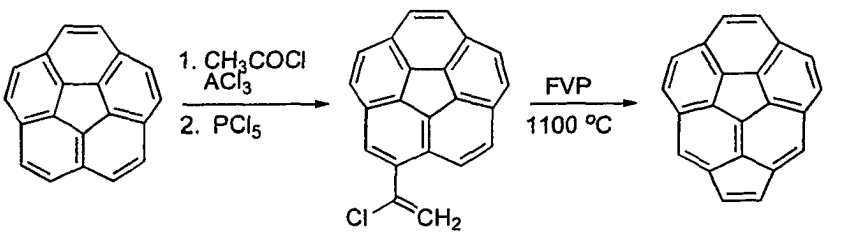
Other systems,[1.5-1.9] seen in **Scheme 1.1.3**, have been successful in producing corannulene when exposed to pyrolytic conditions but none have resulted in significant improvement in yield.

The first expansion toward larger semi-buckminsterfullerenes was accomplished by Abdourazak and Rabideau[1.10] here at LSU, whereby an ethylene bridge was added to corannulene (**Scheme 1.1.4**).



Scheme 1.1.4

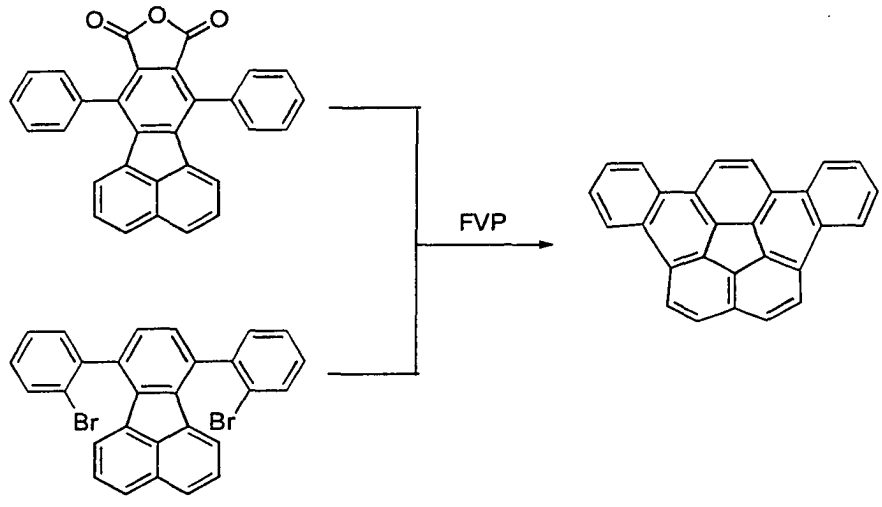
This small addition was enough to conformationally prohibit this molecule from undergoing the bowl-to-bowl inversion that is observed in the case of corannulene itself. An interesting alternate synthesis was accomplished by Scott and coworkers[1.11] shown in **Scheme 1.1.5**.



Scheme 1.1.5

Corannulene itself was acylated, converted to the corresponding chlorovinyl derivative, and then re-pyrolyzed to afford cyclopentenocorannulene.

Further progress was made as Scott and coworkers developed two synthetic sequences for the production of dibenzocorannulene[1.11-1.12] as shown in **Scheme 1.1.6**. The first of these involved the pyrolysis of an anhydride. It is presumed that the molecule loses carbon dioxide and carbon monoxide to produce an aryne intermediate that eventually cyclizes to form the resultant product.

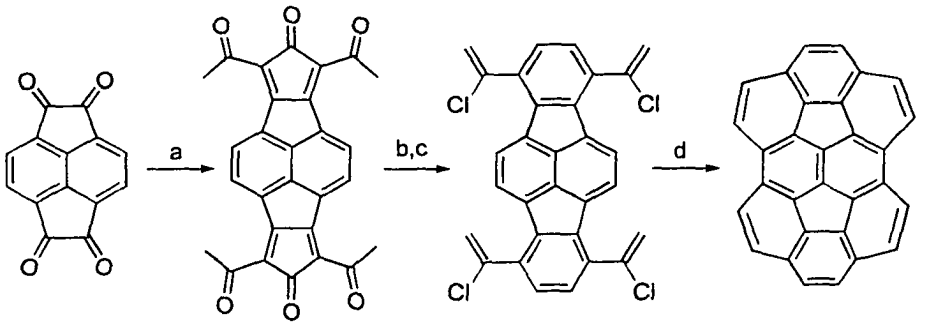


Scheme 1.1.6

The second sequence employed the trapping of aryl radicals formed from homolytic bond cleavage of the carbon-bromine bonds to form dibenzocorannulene.

A major advancement was made when Abdourazak and Rabideau pushed the limits of possibility with the synthesis of the first semi-buckminsterfullerene representing exactly half of coveted C_{60}. (**Scheme 1.1.7**).[1.13] The route required that 1,2,5,6-tetraketopyracene[1.14] be developed analogous to acenapthenequinone in

Scott's synthesis of corannulene. The idea tested the limits as to how many ring closures could occur during pyrolysis.

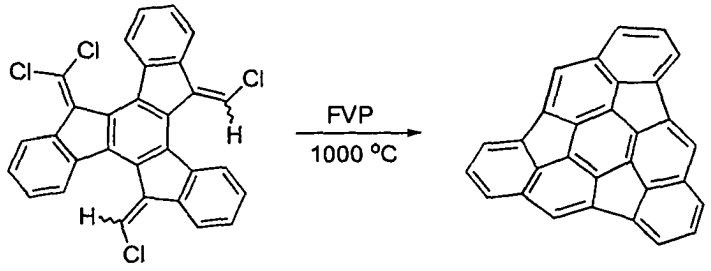


(a) 2,4,6-heptatrione, glycine; (b) norbornadiene; (c) PCl_5; (d) flash vacuum pyrolysis 1000 °C

Scheme 1.1.7

The maximum number of closures up until that time had been two. With this result, that maximum had now been expanded to four ring closures.

One year later Rabideau and coworkers had synthesized another semi-buckminsterfullerene possessing thirty carbon atoms (**Scheme 1.1.8**).[1.15]

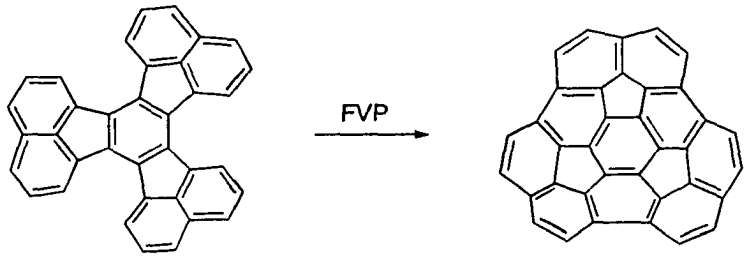


Scheme 1.1.8

The first C_{30} cannot couple to form all of the pentagons and hexagons that make up C_{60} directly because it is not an exact half of C_{60}. However, this C_{30} has the potential, if ever produced in quantities sufficient for further work, to afford

buckminsterfullerene itself through a direct intermolecular coupling of two of these molecules.

To date, the largest of all of the known fullerene fragments was synthesized by Scott and co-workers in 1996.[1.16] As shown in **scheme 1.1.9**, the method was simply flash vacuum pyrolysis of the commercially available decacyclene at between 1200 °C and 1300 °C.



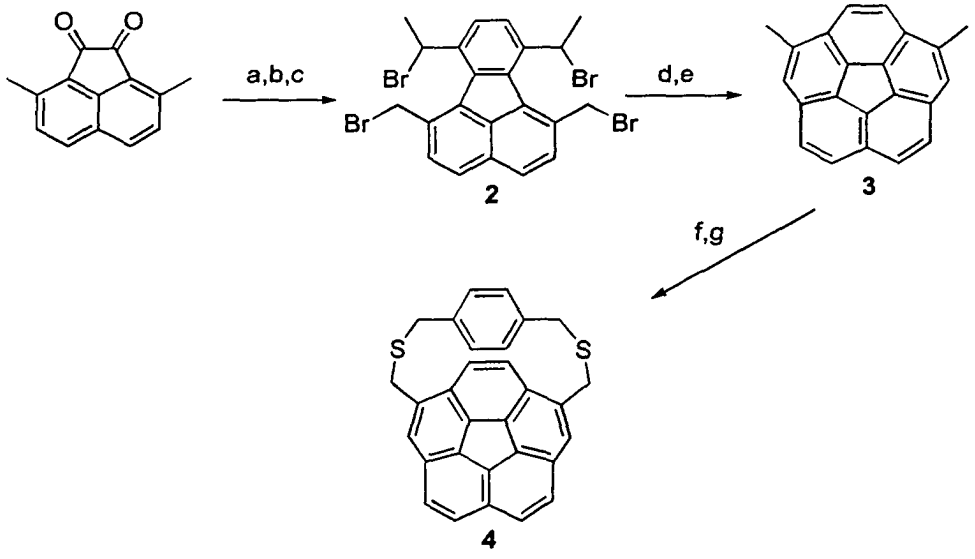
Scheme 1.1.9

Pyrolysis of decacyclene to yield $C_{36}H_{12}$ was previously attempted by both Scott's and our group at 1100 °C only to afford decacyclene unchanged. This truly remarkable molecule with its highly symmetrical "tri-corannulene fused" structure represents 60% of the surface of buckminsterfullerene itself.

Several derivatives of corannulene have been synthesized but all of them involved "post-pyrolytic"chemistry except for the first corannulene cyclophane shown in **scheme 1.1.10**. Siegel and co-workers[1.17] at the University of California at San Diego synthesized this cyclophane starting from dimethylacenapthenequinone, a known but not easily accessible compound. Knoevenagel condensation with 4-heptanone followed by a Diels-Alder reaction with norbornadiene and NBS bromination afforded **2**. Coupling of the two

methylene groups was surprisingly accomplished in 33% yield. This was followed by rearomatization with DDQ to give **3** in 55% yield.

Bromination of **3** with NBS followed by treatment with 1,4-bis(mercaptomethyl)-benzene and potassium tert-butoxide yielded the novel corannulene cyclophane (**4**) in 40% yield.



(a) 4-heptanone, KOH; (b) norbornadiene, acetic anhydride; (c) NBS, benzoylperoxide, $h\nu$; (d) $TiCl_3$, $LiAlH_4$; (e) DDQ; (f) NBS, benzoylperoxide, $h\nu$; (g) potassium tert-butoxide, 1,4-bis(mercaptomethyl)benzene

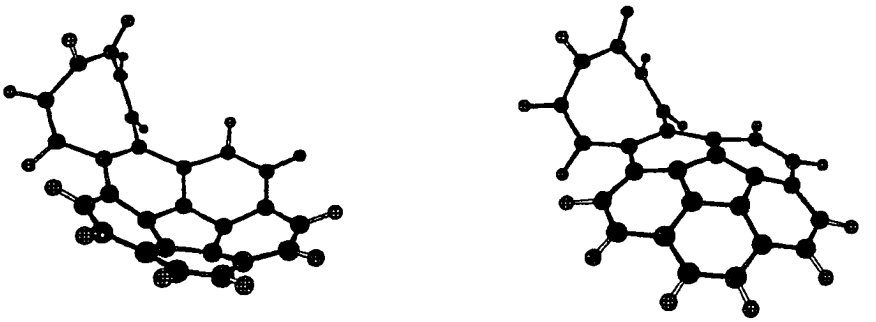
Scheme 1.1.10

It is amazing to see the many advances that have been made in this relatively new area of organic chemistry in just under fifteen years. The work that has been summarized in these few pages is but a preface to what may lie ahead in the future for fullerene related chemistry.

1.2 Results and Discussion

1.2.1 Cyclooctatetraene Annulated Corannulene.

Among the derivatives of corannulene that now exist only a few, such as dibenzocorannulene and cyclopentenocorannulene, are annulated. As corannulene itself has a curved surface, it would be interesting to incorporate another curved surface entity into its structure. Corannulene is known to undergo bowl-to-bowl inversion and when annulated becomes conformationally locked. If the annulated species were to be curved like cyclooctatetraene, it would be quite interesting to learn which conformation, either concave/convex or concave/concave, would be most abundant.(**Figure 1.2.1.1**)

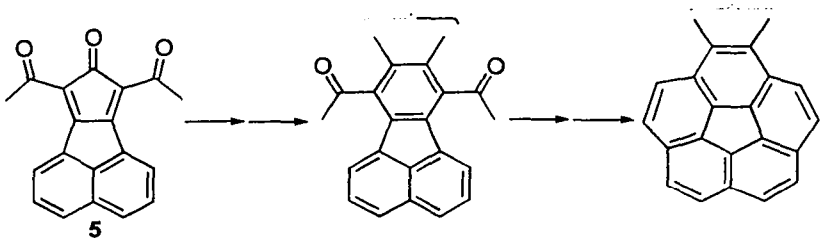


Concave/Concave Concave/Convex

Figure 1.2.1.1

In addition, the question of possible metal complexation of these conformations and where they would prefer to bind would need to be addressed as there has been no conclusive evidence to date on the formation of a corannulene metal complex.

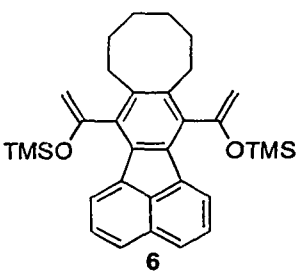
As demonstrated by Scott et al,[1.18] triketone **5** can serve as a useful intermediate in the synthesis of corannulenes (**Scheme 1.2.1.1**).



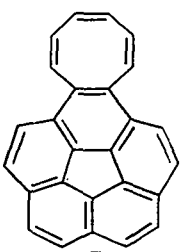
5

Scheme 1.2.1.1

In an attempt to develop a synthesis of a cyclooctatetraene annulated corannulene (**7**), we reacted cyclooctene with the triketone **5** to prepare **6** for pyrolysis. Unfortunately, under pyrolytic conditions, compound **6** loses the eight-membered ring.



6

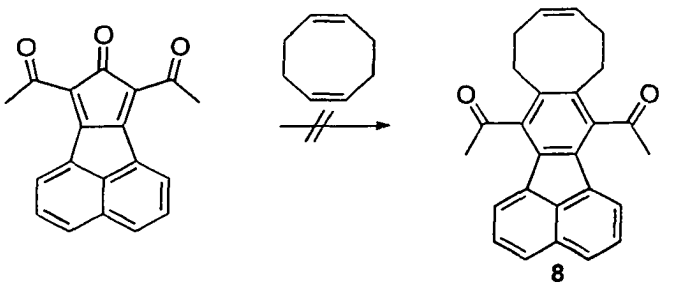


7

Hence, we decided to incorporate more unsaturation at the stage of the Diels-Alder reaction with the idea of completely unsaturating the eight-membered ring before pyrolysis. The stronger vinyl bonds might be more resistant to rupture under the conditions of flash vacuum pyrolysis.

When cyclooctadiene was employed in the Diels-Alder reaction, the expected product **8** was not formed. The ^{1}H NMR showed nine different signals

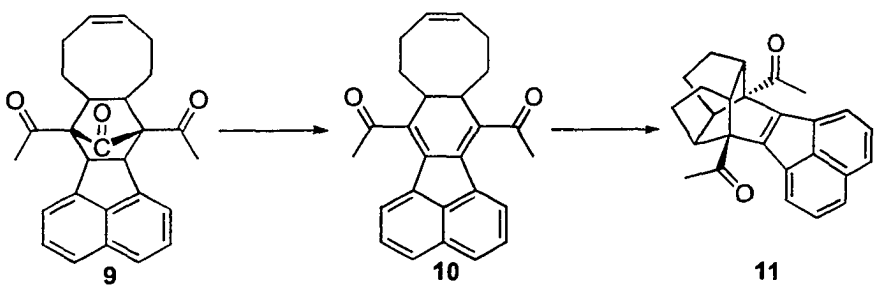
instead of only seven that would be required by symmetry and flexibility for the desired product. In addition, no vinyl protons were observed and there were two methyl peaks instead of one.



8

In order for these conditions to be met, the molecule must have undergone some reaction that would eliminate the double bond in the eight-membered ring, destroy the symmetry of the molecule, and cause a significant rotational barrier such that the methyl protons would be unable to yield one averaged signal.

The solution to the puzzle is shown in **Scheme 1.2.1.2**. The initial Diels-Alder reaction yields a bicyclic intermediate **9** still having the center carbonyl



9 10 11

Scheme 1.2.1.2

intact. After loss of one molecule of carbon monoxide, an electron poor diene **10** is formed. Normally this intermediate would be unable to react further. However,

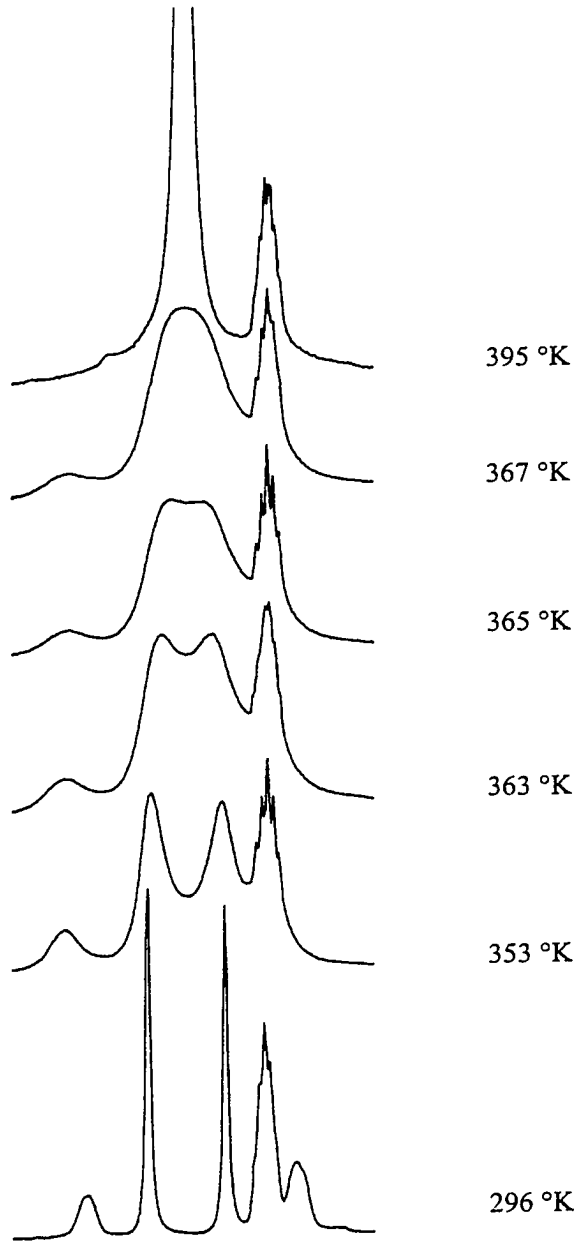


Figure 1.2.1.1

due to the saddle shape of the cyclooctene ring, the p orbitals are within range to react via another inverse electron demand Diels-Alder reaction to form cage compound **11** that satisfies all the conditions necessary to resolve the ^{1}H NMR. Confirmation of this cage structure would be complete if one could observe the two methyl signals coalesce into one and then measure the rotational barrier. This was accomplished by obtaining ^{1}H NMR spectra over a range of temperatures using a 400 MHz spectrometer. The results of our efforts are shown in **Figure 1.2.1.1**. Coalescence is reached at 367 °K. The barrier for rotation is defined as $\Delta G^{\neq}$ and given by the following equation:[1.19]

$$\Delta G^{\neq} = (19.13)(T_c)\{9.97 + \log_{10}(T_c/\Delta\nu)\}(J/mol)$$

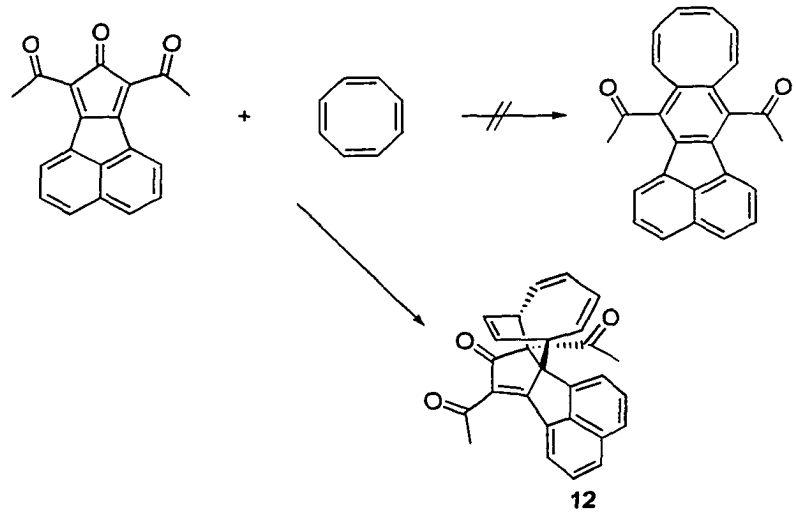
where Tc = coalescence temperature
$\Delta\nu$ = chemical shift difference in Hz

Hence barrier of rotation for this molecule is 78.1 kJ/mol.

The cage compound though interesting did not yield the desired intermediate. Therefore, a different dienophile would have to be found in order to accomplish this aim. The first that came to mind was cyclooctatetraene since the resultant product would need no further modification of the eight-membered ring unlike the previous case. It is known that cyclooctatetraene exists in a conformational equilibrium (**Scheme 1.2.1.3**).[1.20]

Scheme 1.2.1.3

If the double bond in the cyclobutene ring of the minor component of this equilibrium could be trapped, a subsequent conformational rearrangement would yield the desired product.**(Scheme 1.2.1.4)**



Scheme 1.2.1.4

Unfortunately, the desired product was not formed but rather **12** was produced by what seemed to be a normal electron demand Diels-Alder reaction. Characterization of **12** was by no means accomplished immediately. ^{1}H MNR showed five different types of aromatic protons, five different types of vinyl protons, and four different types of aliphatic protons. This is twice the number of protons that would be required by symmetry for the desired product. Having had a situation where a somewhat symmetrical cage was formed previously, it was initially thought that an analogous situation had occurred here as well. The idea persisted until the crystal structure was obtained which is shown in **Figures 1.2.1.2** and **1.2.1.3**.

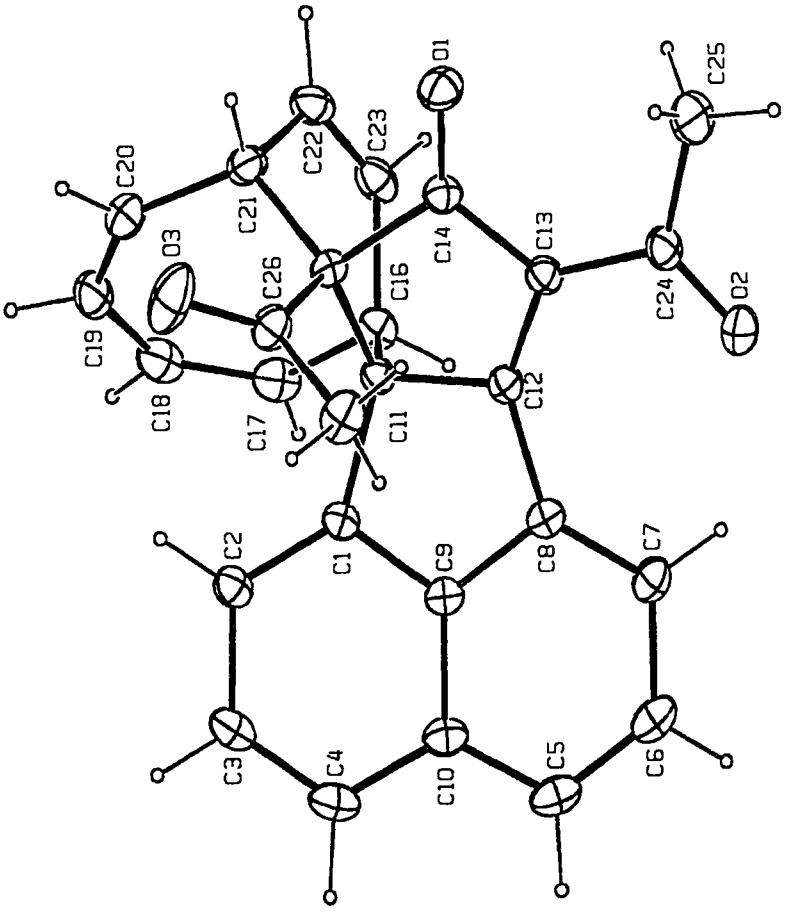


Figure 1.2.1.2

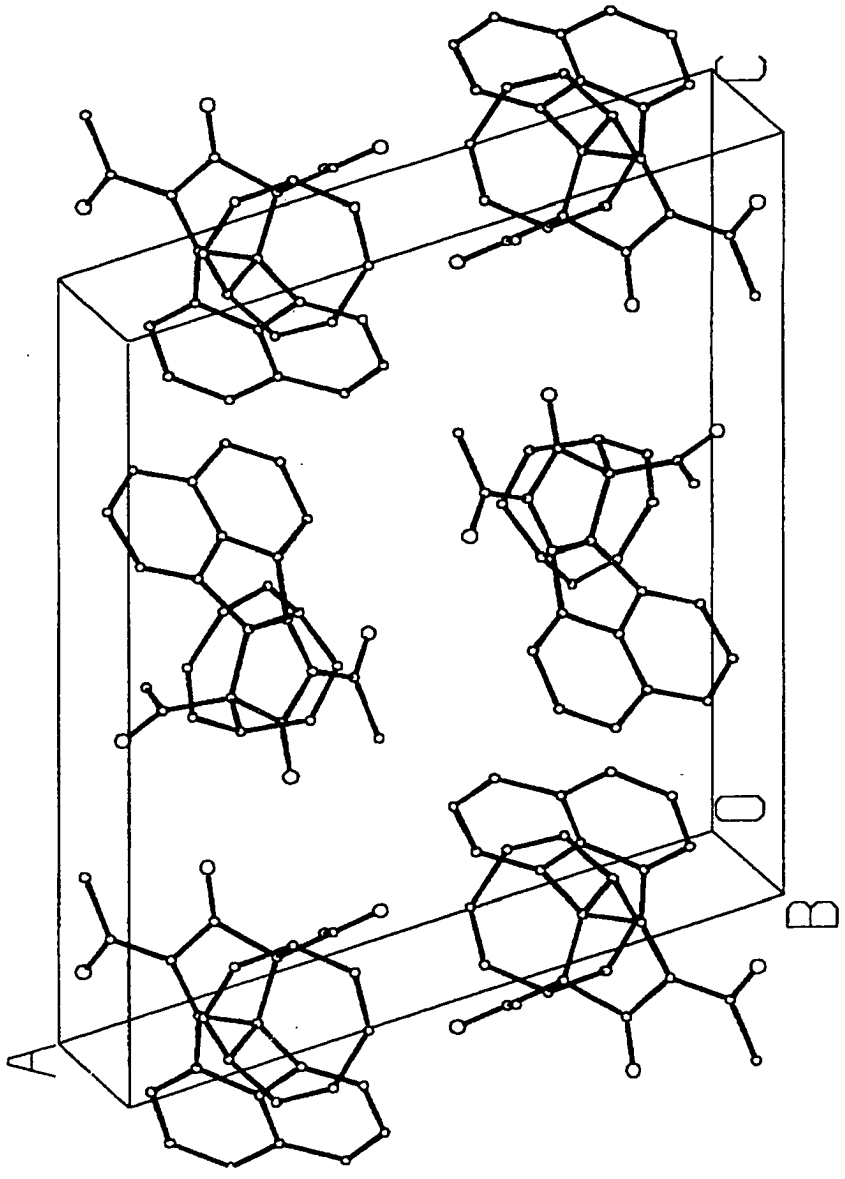
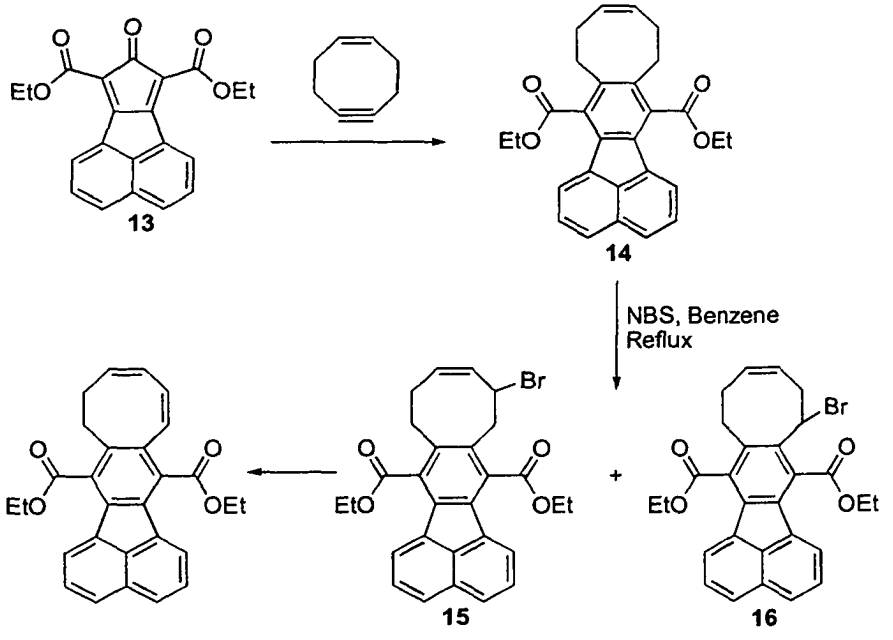


Figure 1.2.1.3

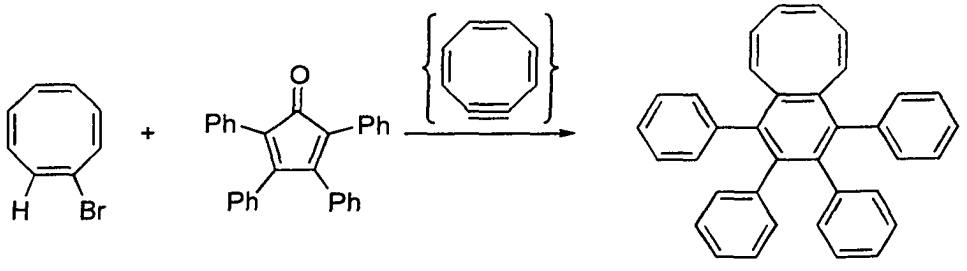
Failure in the previous attempt to attach the eight membered ring was caused by the creation of a second diene and the availability of a second double bond to yield the first cage molecule. It was proposed (**Scheme 1.2.1.5**) that if the



Scheme 1.2.1.5

newly formed six-membered ring could aromatize itself first, the opportunity for a second Diels-Alder reaction would then be eliminated. Accomplishing this task could be realized by the formation of 1-cyclooctene-5-yne followed by treatment with a diene **13**. Allylic bromination of the resultant product **14** via treatment with N-bromosuccinimide yielded a monobrominated mixture of **15** and **16** that were inseparable by standard methods. Elimination of the bromines with Li_2CO_3 and LiCl yielded a mixture of products including a potentially useful intermediate. However, due to low yields we decided to move on to a better route.

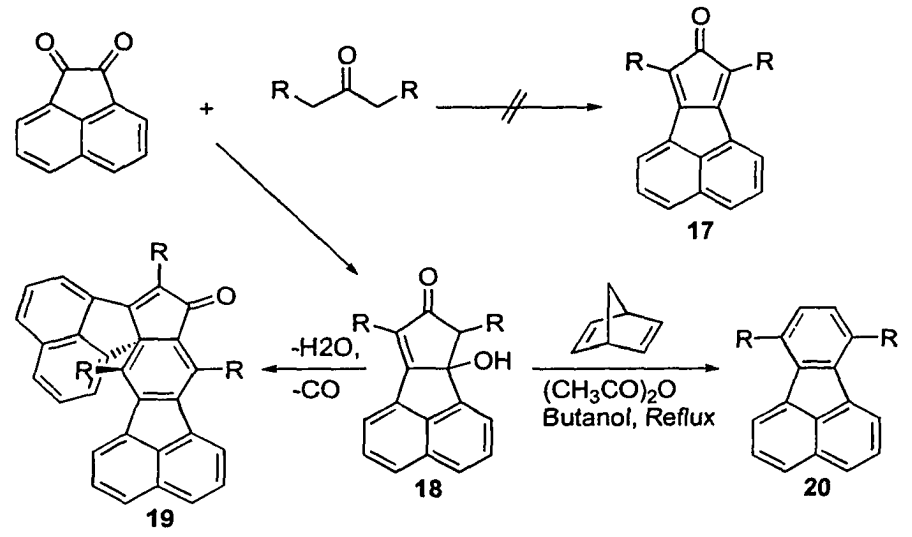
The solution to the problem now seemed to point in one direction and that was to form a cyclooctatriene-yne dieneophile in situ and trap it with our diene **13**. Lankey and Ogliaruso had accomplished a similar cycloaddition by treating bromocyclooctatetraene with potassium tert-butoxide and tetracyclone in tetrahydrofuran at 30 °C over a 70 hour time period.[1.21]



Unfortunately, the diene **13** when treated with potassium tert-butoxide is destroyed much faster than the intended elimination of HBr from the bromocyclo-octatetraene. This result though frustrating was not surprising given that compounds having the 2,4,6-trione structure are known to be quite labile.

It seemed that just as we had found a suitable dienophile, our diene had failed. Therefore we then set out to replace the acetyl and ester groups with either methyl or ethyl groups with hopes of creating a diene that would be less sensitive upon treatment with base. Attempts to condense 3-pentanone and 5-heptanone with acenapthaquinone failed to yield the desired diene **17** but gave the carbinol **18** instead. **Scheme 1.2.1.6**

It is known that dehydration of **18** leads to the formation of a dimer which subsequently loses carbon monoxide to form **19** when heated above 45 °C.[1.22] It is



Scheme 1.2.1.6

also known that when **18** is refluxed in butanol and norbornadiene with acetic anhydride that the subsequent Diels-Alder adduct **20** is formed.[1.23] This information while interesting is not applicable in this situation since removal of the carbinol requires a temperature of at least 89 °C and dimerization of the cyclooctatriene-yne occurs above 30 °C.[1.24]

Since we had concerns that the 8-membered ring would fail to remain intact during pyrolysis and since incorporation of that unsaturated ring was becoming quite difficult, we decided to discontinue the project.

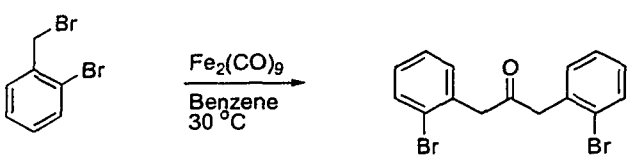
1.2.2 Synthesis of $C_{32}H_{12}$

To date all syntheses of known bucky-bowls with the exception of Siegel's method[1.17] of synthesizing dimethylcorannulene and the original Barth and Lawton method,[1.12] employ pyrolysis of various functional groups. Most of the

represented groups, though stable at room temperature, become quite labile when subjected to normal pyrolytic processes. This reactivity makes these precursors susceptible to polymerization as well as many other possible side reactions. Having said this, it is not surprising that the yield of many of these reactions is at best very low. If one could tailor a functional group or system that would be totally unreactive at lower temperatures while being reactive enough at pyrolytic conditions, it might be possible to improve the yield of the resultant compound to an acceptable level.

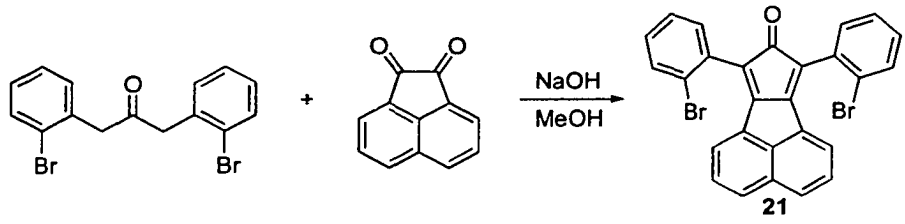
Scott had incorporated a bromophenyl group which upon pyrolysis closed two six-membered rings to form dibenzocorannulene.[1.12] It was this idea that led me to further investigate the possibility of incorporating a bromophenyl derivative into a modified synthesis of corannulene in hopes of forming tribenzocorannulene.

Synthesis of the necessary 2-bromophenyl ketone was accomplished through the method developed by Bennett and Newmann[1.25] shown in **Scheme 1.2.2.1**. This convenient two-step method was a vast improvement over an alternate five-step synthesis which employed more classical methods.



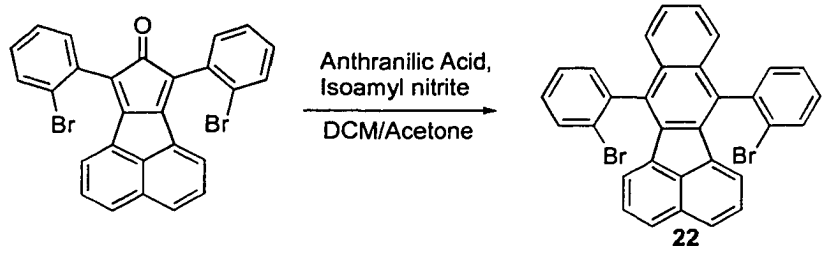
Scheme 1.2.2.1

Condensation of the 2-bromophenyl ketone with acenapthenequinone in methanol with a catalytic amount of sodium hydroxide afforded **21** in 96% yield **(Scheme 1.2.2.2)**.

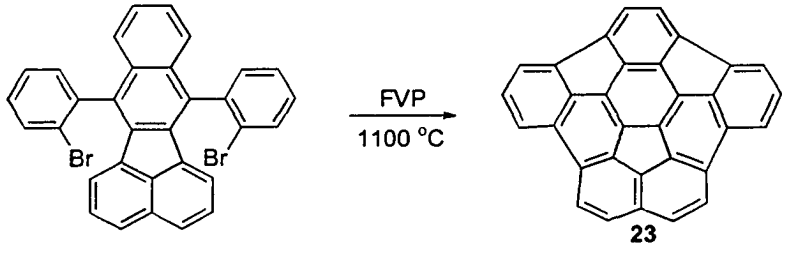


Scheme 1.2.2.2

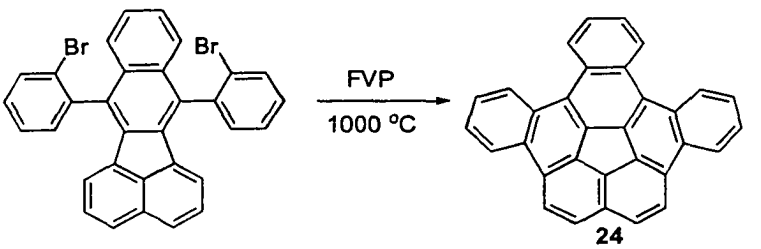
Compound **21** was then reacted with benzyne, generated in situ from anthranilic acid and isoamyl nitrite in a dichloromethane/acetone mixture, to give **22** in 77% yield.



Adduct **22** (5.1 grams) subsequently underwent flash vacuum pyrolysis at 1000 °C in 200 mg portions to yield 5 mg of (**23**).



The formation of **23** was quite surprising as this compound was not my intended goal. My intended goal was to synthesize tribenzocorannulene **24** shown in **Scheme 1.2.2.3**.



Scheme 1.2.2.3

Up to this point, simultaneous closure of four rings, two six-membered aromatic rings and two five-membered rings was inconceivable. This compound, whose calculated structure is shown in **Figure 1.2.2.1**, is the only example of the formation of multiple five-membered rings via pyrolytic processes. All other

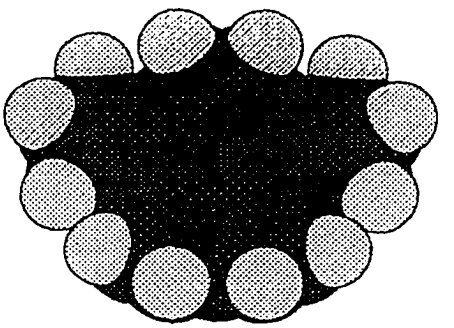
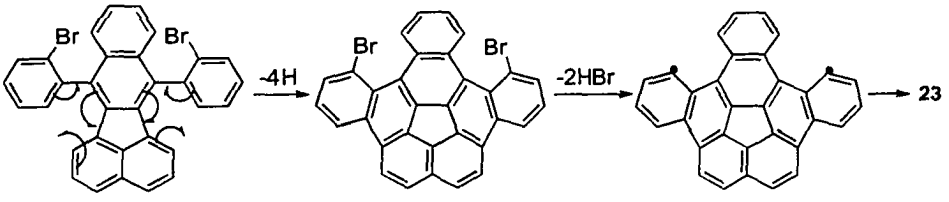


Figure 1.2.2.1

previous precursors included preformed five-membered rings. This result is quite significant since it indicates that precursors to form C_{60} would not require previously formed five-membered rings to be successful. As a result, this precedent allows the synthetic chemist some variability in designing novel precursors toward the synthesis of C_{60}.

A possible mechanism for the conversion of **22** to **23** is shown in **Scheme 1.2.2.4**. Initial cyclodehydrogenation could form one set of rings while subsequent loss of bromine could produce aryl radicals that could then result in the formation of the second set of rings yielding **23**. The issue as to which of these processes occurs first could not and probably will not ever be determined due to the difficulty in trapping possible reaction intermediates that may be formed at 1000-1100 °C.



Scheme 1.2.2.4

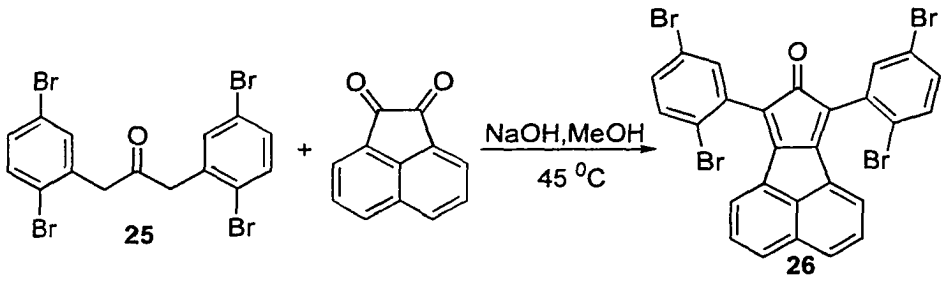
1.2.3 An Alternate Route

Although we had synthesized a novel compound, the yield was rather low. In hopes of improving the yield, this methodology was extended by incorporating two additional bromine atoms in the pyrolytic precursor. If the previously mentioned mechanism were true, then it would be logical to conclude that if we incorporated additional halides in strategic positions that the number of aryl radicals would be significantly increased thereby increasing the odds of ring closure.

As in the first synthesis it was necessary to incorporate the bromine atoms in the correct positions on the benzyl ketone that would later be condensed with acenapthenequinone. The halides would need to be placed in the second and sixth positions on the phenyl rings in order for formation of the aryl radicals to be

optimized for the subsequent ring closures. Here again, the method for accomplishing this task was that of Bennett and Neumann[1.25] with a few small modifications in the work-up. So 2,6-dibromobenzylbromide was reacted with di-ironnonacarbonyl in benzene at 30 °C for 24 hours to afford the 2,6-dibromophenyl ketone. Unfortunately, condensation of this material with acenapthenequinone failed to give the expected product due to steric interference.

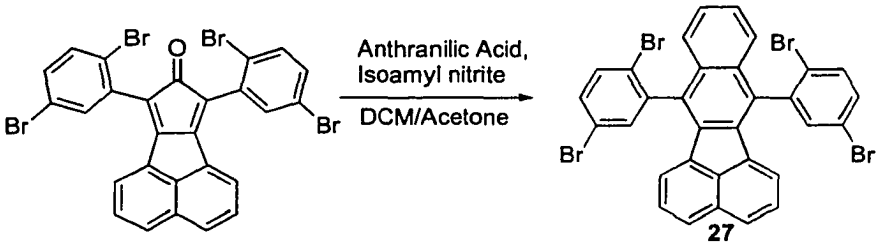
Rather than give up the idea, we speculated that it might not be necessary to have the halides in the exact positions where the closures would need to take place



Scheme 1.2.3.1

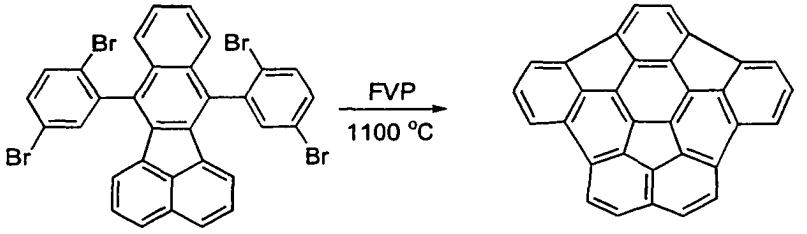
in order to form the desired product. Therefore, we decided to use 2,5-dibromobenzylbromide to form the required ketone. The subsequent 2,5-dibromobenzyl ketone **25** was obtained in 85% yield and then successfully condensed with acenapthenequinone and sodium hydroxide in methanol at 45 °C to give **26** as seen in **Scheme 1.2.3.1.**

The resultant ketone, as shown in **Scheme 1.2.3.2**, was reacted as before with benzyne generated in situ from anthranilic acid and isoamyl nitrite in a dichloromethane/acetone mixture to give **27** in 64% yield.



Scheme 1.2.3.2

This material was then subjected to flash vacuum pyrolysis at 1100 °C and 3.4 mg of **23** was obtained from 3.6 grams of starting material. Unlike the pyrolysis of the



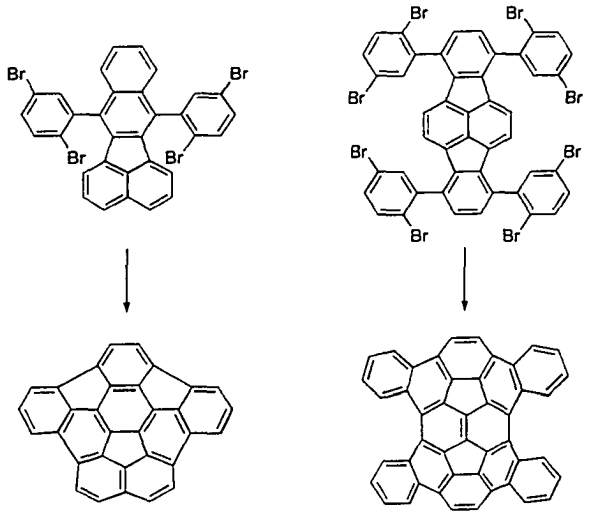
first precursor, the tetrabromo compound did not sublime with ease. I feel that it is for this reason that no major improvement in yield was observed and not because the additional halides failed to facilitate more facile ring closures. However some improvement was achieved as separation of the product was facilitated by the lack of other products that were produced using the original synthesis of $C_{32}H_{12}$.

1.2.4 Attempted Expansion to $C_{46}H_{16}$.

It is the ultimate dream of every synthetic chemist who has worked in the sub-category of organic chemistry known as polynuclear aromatic hydrocarbons to eventually synthesize buckminsterfullerene via classical methods. This requires that precursors via pyrolytic processes must contain at least sixty carbon atoms. As previously mentioned, the buckybowl possessing the highest number of carbon

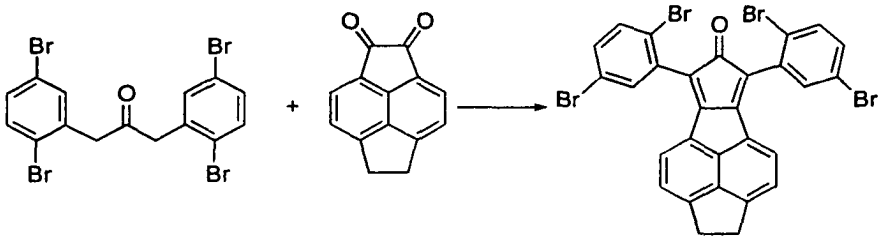
atoms now stands at thirty-six. It must be noted that as one adds more and more carbon atoms the ability of the particular precursor to sublime and then close to form these buckybowls decreases significantly.

If one considers the system that was successful in forming $C_{32}H_{12}$ as a model, then development of similar sites of reactivity on the opposite end of the



molecule would result in a precursor that could potentially yield $C_{46}H_{20}$. This new polynuclear aromatic compound would represent 70% of the surface of buckminsterfullerene and bring us one step closer to reaching that lofty goal of sixty carbon atoms arranged in a sphere.

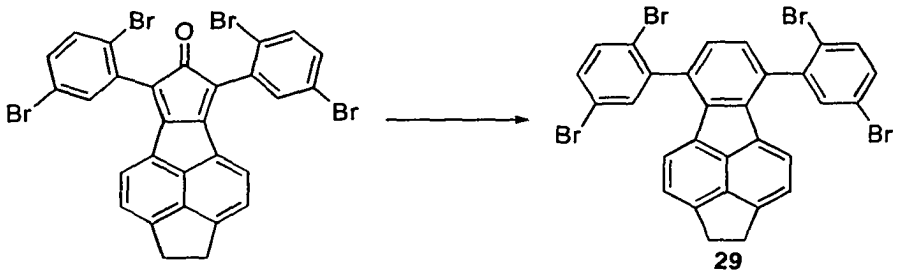
The first step in the synthesis of $C_{46}H_{20}$ involved making **28**. This was accomplished by condensing 2,5-dibromobenzylketone with 1,2-diketopyracene in methanol at 45 °C for 24 hours using a catalytic amount of sodium hydroxide in 85% yield. The ^1H NMR spectrum shows multiplets centered at 7.60 ppm,



28

7.42 ppm, and a singlet at 3.54. These signals integrate for 4, 6, and 4 protons respectively. The ^{13}C NMR shows seven C-H carbons at 148.25, 134.87, 134.78, 132.77, 121.94, 121.93, and 32.59 ppm. Theoretically, one should only observe six signals; five for the aromatic C-H carbons and one for the aliphatic carbon. The signals found at 134.87 and 134.78 ppm arise from slightly different rotational isomers about the bond connecting six membered ring to the five membered ring containing the ketone and might indicate formation of chirality. These signals would most likely collapse into one signal if a lower field instrument had been used to record the spectrum or if the NMR experiment would have been carried out at an elevated temperature. The signals observed at 198.67, 158.80, 144.57, 138.61, 134.52, 126.97, 125.50, 122.78, and 119.95 ppm represent the quaternary carbons and are consistent with the theoretical number of carbons required for this molecule. Some speculation exists as to whether the signal at 198.67 ppm truly identifies the carbonyl carbon or is only a glitch in the spectrum. To insure that the carbonyl functional group was present, an IR spectrum of the compound was taken and a C-O stretching frequency was observed at 1706.6 cm^{-1}.

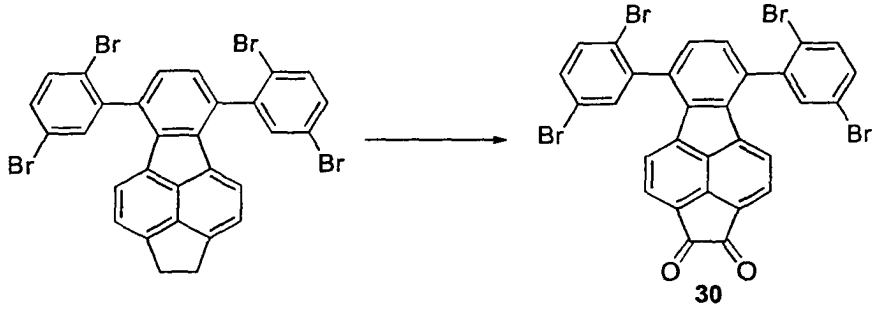
Treatment of **28** with an excess of norbornadiene in xylenes over a five day period afforded **29** in 45% yield. The ^{1}H NMR of this compound is totally



29

consistent with what one would expect to observe for this structure. ^{13}C NMR shows C-H signals at 134.64, 134.59, 134.30, 134.07, 132.67, 127.79, 124.80, 121.20, and 32.52 ppm. Quaternary carbon signals are found at 146.84, 143.77, 143.73, 138.19, 136.62, 135.86, 131.43, 122.71, 122.68, 121.56, and 121.20 ppm. There are more signals both for C-H and quaternary carbon than are theoretically required and we maintain that these are doubled due to rotational isomerism. A fast atom bombardment mass spectrum yield an average m/z ratio of 695.4 and shows an isotope pattern consistent with four bromine atoms.

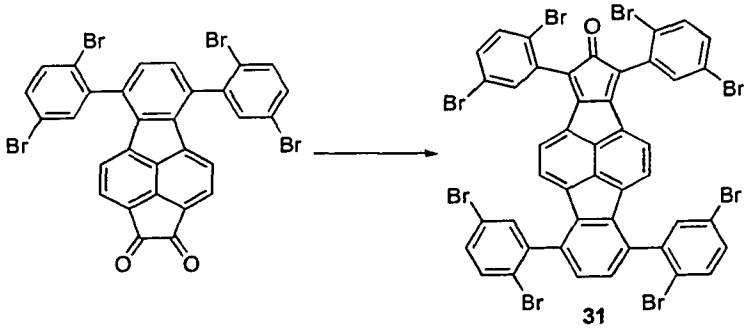
Conversion of **29** to the diketone **30** via treatment with benzeneseleninic anhydride in chlorobenzene was done over a 48 hour time period. After standard work-up and purification via column chromatography the material was obtained in 77% yield.



30

The spectral data are quite consistent with the proposed structure and are confirmed by carbon/hydrogen analysis.

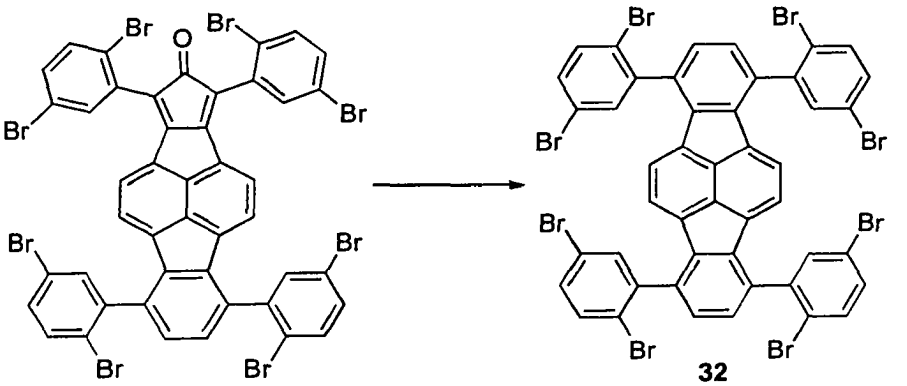
The diketone was treated in an analogous manner as was the 1,2-diketopyracene. Condensation with 2,5-dibromobenzylketone in methanol at 45 °C for 24 hours afforded **31** in 69% yield.



31

^{1}H NMR shows two multiplets centered at 7.65 and 7.42 ppm which integrate for twelve and four protons respectfully, as well as a doublet-of-doublets at 7.18 ppm that integrates for two protons. ^{13}C NMR reveals nine C-H protons at 138.13, 137.13, 134.81, 134.06, 133.15, 129.57, 125.52, and 121.24 ppm. The ninth C-H carbon can be observed as a shoulder to the signal at 134.81 ppm. Of the fifteen quaternary carbons that are required for this molecule, twelve can be observed. These are found at 156.36, 142.73, 141.28, 138.31, 134.44, 133.83, 130.33, 130.01, 122.75, 122.45, 122.13, and 121.82 ppm. The signal for the ketone, however, is noticeably absent. Fast atom mass spectrometry shows an average mass to charge ratio of 1213.9 which is exactly the mass of the desired product. Moreover, the mass spectrum shows an isotope pattern that is consistent with a molecule containing eight bromine atoms.

1,4,7,10-Tetrakis(2,5-dibromophenyl)-indeno[1,2,3-cd]fluoranthene (**32**) was made via treatment of **31** with norbornadiene in refluxing bis(2-ethoxyethyl) ether over 12 hours in 27% yield.



32

This compound was also successfully produced when the reaction was done in refluxing xylenes over a period of one week. Unfortunately, the yield was of the same order as when done over a twelve-hour period in bis(2-ethoxyethyl) ether. The low yield can be attributed to the poor solubility of the compound in most organic solvents.

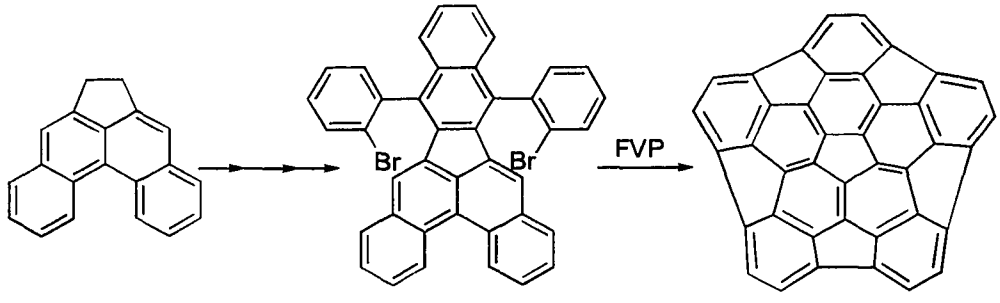
^{1}H NMR shows three multiplets at 7.73, 7.13, and 6.34 ppm that integrate for twelve, four, and four protons respectively. The ^{13}C NMR shows fourteen signals that are all found in the region expected for aromatic carbons. However, due to the low solubility of the material, it is not possible to identify all of the carbons required to prove the given structure. Fast atom bombardment mass spectrometry shows the necessary average mass to charge ratio of 1211.7 as well as identifies every single isotope peak that this molecule requires.

Pyrolysis of **32** at 1100 °C was attempted several times in the hopes of producing $C_{46}H_{20}$. Our efforts, unfortunately, did not lead to the desired target mostly due to the material's unwillingness to sublime into the hot zone.

1.2.5 Attempted Synthesis of a Novel Fullerene Fragment Building Block

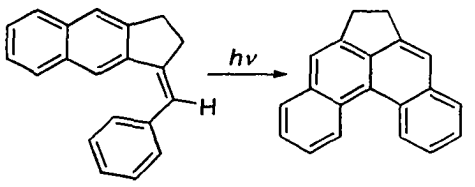
After having pushed our previous pyrolytic precursors beyond the limits of sublimation with the attempt to synthesize $C_{46}H_{20}$, we began considering possible systems that we could develop using what we had learned from the synthesis of $C_{32}H_{12}$.

System **33** seemed to fit these criteria. If we could find a high yield and relatively inexpensive way to produce **33**, it might give us the ability to do further work in developing precursors like **34**. These new precursors might eventually lead to additional novel fullerene fragments such as $C_{40}H_{10}$ shown below.



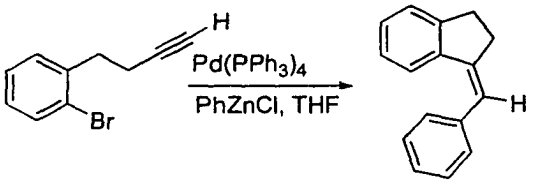
33 **34** $C_{40}H_{10}$

Compound **33** had been synthesized through a long and quite laborious procedure.[1.26] It was proposed that if we could synthesize **35**, our key intermediate **33** would be obtainable via an oxidative photocyclization.[1.27]



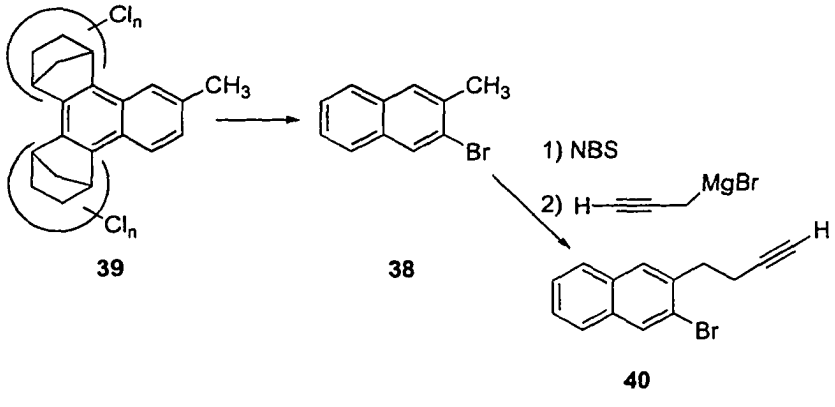
35 **33**

The most direct route to **35** seemed to be provided by Wang et. al[1.28] They had successfully synthesized **36** from **37** via a palladium catalyzed intramolecular coupling reaction done in tetrahydrofuran at room temperature over a period of 10 hours in 51-60% yield.



37 **36**

This method seemed most attractive as the main starting material **38** was known[1.29] and could be produced in large quantities and in high yield from the commercially

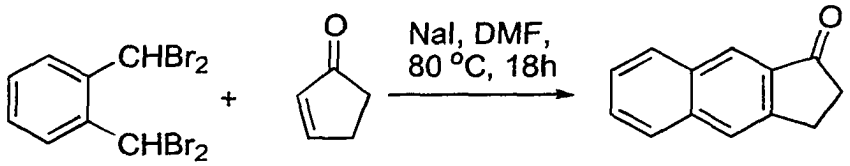


39 **38** **40**

available **39** at low cost. When **39** was treated with NBS and then excess allenylmagnesium bromide, **40** was produced in almost quantitative yield,

analogous to the literature report. However, despite several attempts, the desired product **34** was not formed.

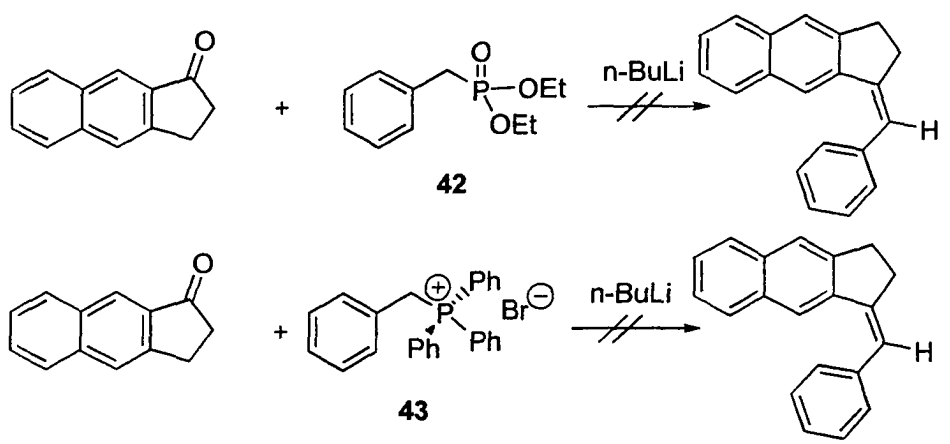
We sought to continue our attempts to synthesize **35**, and therefore decided to use a more classical approach employing Wittig chemistry. Benz[f]indan-1-one (**41**) can be easily synthesized using a procedure developed by Calvin Becker and Professor Mark McLaughlin.[1.30]



41

α,α,α′,α′,-Tetrabromo-o-xylene is treated with sodium iodide and 2-cyclopentenone in dimethylformamide at 80 °C for a period of 18 hours to afford the desired product in 57% yield.

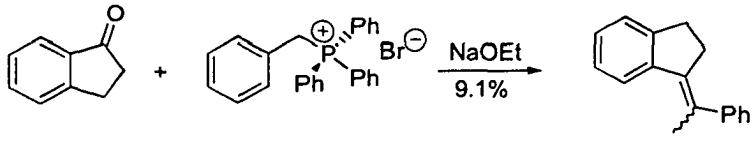
Several attempts at obtaining **35** via treatment of **41** with the corresponding ylides of both diethyl benzylphosphonate (**42**) and triphenylphosphine bromide (**43**)



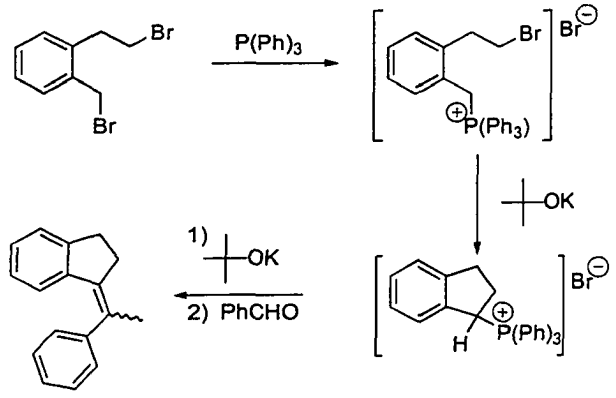
42

43

failed to produce the desired product. These results were not surprising in view of the findings of Witschard and Griffin[1.31] who studied Wittig reactions on various cyclic ketones including indanone in 1964. They treated indanone with the appropriate ylide formed from reacting benzyltriphenylphosphonium chloride with sodium ethoxide. While this did produce **36**, the yield was only 9.1%.

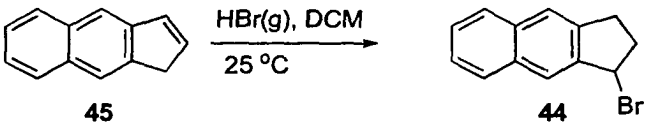


Four years later Bestmann, Hartl, and Haberlein published a report[1.32] in which **36** was produced in 28% yield via a reverse Wittig transformation shown below.**(Scheme 1.2.4.1)**



Scheme 1.2.4.1

Initially this approach seemed quite promising as the required starting material 1-benz[f]indanyl bromide (**44**) had been produced in quantitative yield from 1*H*benz[f]indene (**45**).[1.33] Unfortunately, treatment of **44** with one equivalent of



45 44

triphenylphosphine at 25 °C for a period of 72 hours in benzene did not yield the desired product. Of course, as seen in **Scheme 1.2.4.1**, Bestmann et al.[1,32] did not make their Witting reagent from a cyclopentyl bromide and it may be that our attempts failed due to the tendency of HBr elimination in the latter.

1.3 Conclusions

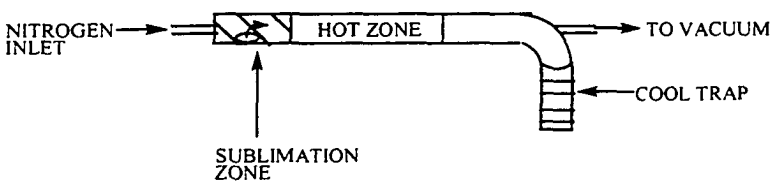
From this series of experiments it was learned that multiple ring closures of various sizes are possible when utilizing multiple aryl radicals generated from halogenated arene rings during flash vacuum pyrolysis. When attempting to improve the yield of such processes, we also learned that there exists a delicate balance between maximizing the number of possible aryl radicals formed from adding additional halides and the sublimability of the material undergoing flash vacuum pyrolysis.

1.4 Experimental

1.4.1 Materials and Methods

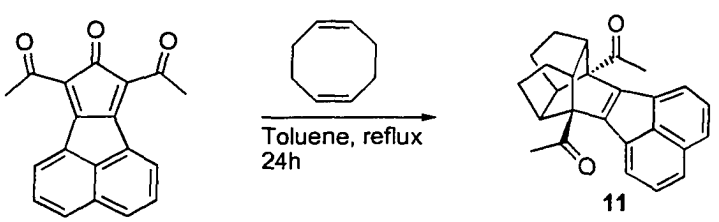
Materials were obtained from commercial sources and used without further purification. All reactions were done under a nitrogen atmosphere. NMR spectra were collected with a Bruker AC-200, AC-250, ARX-300, or AMX-400 in $CDCl_3$ unless indicated otherwise. Chemical shifts are expressed in parts per million downfield from an internal standard of tetramethylsilane. Coupling constants are reported in Hertz. GC/MS data were collected on a Hewlett Packard 5971 mass

spectrometer. High-resolution mass spectrometry was done by the Mass Spectrometry Facility at Louisiana State University. Elemental analyses were done by Oneida Research Services Inc.. Melting points were taken on a MEL-TEMP II capillary melting point apparatus and are reported uncorrected. The silica gel used for liquid chromatography was purchased from Aldrich Chemical Company. Pyrolysis involved sublimation of the starting material under vacuum in a quartz tube, which was carried via a slow flow of nitrogen through a hot zone maintained at 1000-1100 °C as shown below. The products were subsequently collected in a trap cooled to –78 °C using a dry ice/acetone bath and removed by washing this



trap with methylene chloride. The furnace used for flash vacuum pyrolysis was purchased from Kontes Glass Inc.

1.4.2 Synthesis of 5,11c-diacetyl-2,3,3a,4,5,11c-hexahydro-4,1,5-[1]propanyl[3]ylidene-1*H*-cyclopenta[*j*]fluoranthene

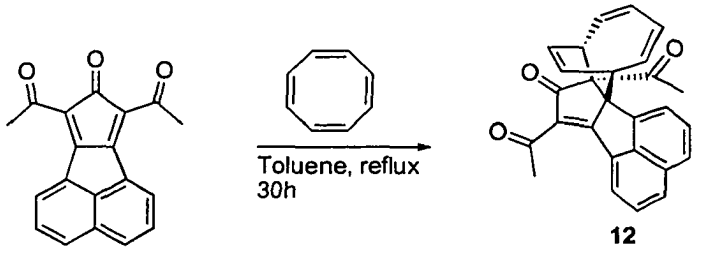


11

In a round-bottomed flask equipped with a reflux condenser and magnetic stirrer were placed 0.100 g of **5**, 42 μL of cyclooctadiene, and 25 mL toluene. The

mixture was stirred at reflux for a period of 22 hours. The reaction was then allowed to cool to room temperature and the yellow precipitate that formed was filtered and washed with ethanol to give 0.097 g of the product in 73% yield: mp 196 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.85(d, J = 8.1 Hz, 2H), 7.55(t, 7.55,2H), 7.41(dd, J = 2.2, 6.9 Hz, 2H), 2.65(s, 1H), 2.60(s, 3H), 2.47(s, 2H), 2.54(s, 3H), 2.28(s, 1H), 1.98(m, 2H), 1.85(m, 2H), 1.57(m, 4H). ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 210.78, 210.52, 174.89, 138.78, 128.79, 127.83, 127.65, 122.37, 110.56, 63.40, 47.01, 45.60, 44.36, 42.92, 28.42, 25.62, 25.40, 24.71, 24.22, 24.15. GCMS (m/z, rel. int.) 368 (15), 325 (8), 281 (18), 259 (13), 215 (15), 207 (100). Anal. Calcd for $C_{26}H_{24}O_2$: C, 84.75; H, 6.57. Found: C, 84.42; H, 6.79.

1.4.3 Synthesis of 7,8a-diacetyl-9,14-dihydro-9,14-ethenocycloocta-[1,5]cyclopent[1,2-*a*]acenaphthylen-8(8aH)-one

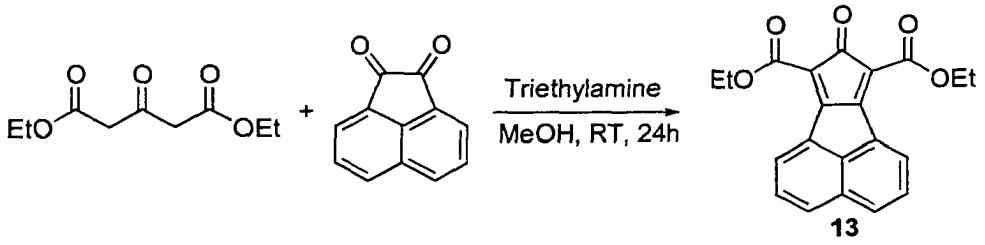


12

In a 3-necked 100 mL round-bottomed flask were placed 2.0 g of **5**, 1.0 mL of cyclooctatetraene, and 50 mL of toluene. The reaction was allowed to reflux for 30 hours during which time an additional 1mL portion of cyclooctatetraene was added. The reaction was stopped and allowed to cool to room temperature when all of the starting material had been consumed as shown by thin layer chromatography. After removal of the solvent the residue was separated over silica gel using toluene/methylene chloride 5:1 to afford 0.735 g of the product in 26% yield as a

yellow solid: mp 208 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.81(d, J = 7.28 Hz, 1H), 8.10(d, J = 8.13 Hz, 1H), 7.73(m, 2H), 7.51(t, 1H), 7.24(d, J = 7.1, 1H), 6.60(t, 1H), 6.13(m, 1H), 5.85(m, 1H), 5.67(m, 2H), 5.16(t, 1H), 4.00(t, 1H), 2.82(m, 1H), 2.58(s, 3H), 1.51(s, 3H). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 201.71, 200.08, 194.75, 191.42, 137.31, 134.56, 132.43, 131.45, 129.11, 128.86, 128.35, 127.83, 126.51, 124.96,124.89, 124.45, 120.85, 85.76, 79.83, 64.76, 45.17, 36.60, 30.33, 27.57. GCMS (m/z, rel. int.) 364(16), 307(13), 286(66), 271(100), 243(45), 200(58), 138(17), 100(25). Anal. Calcd for $C_{27}H_{20}O_3$: C, 82.6; H, 5.1. Found: C, 82.2; H, 5.1. Crystallographic data for this compound are shown in **Tables 1.4.2.1-1.2.4.6.**

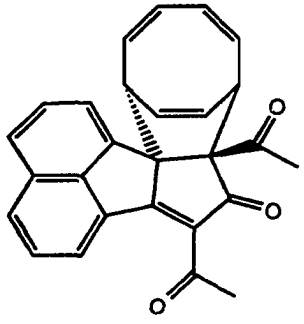
1.4.4 Synthesis 8-oxo-8H-cyclopent(a)acenaphthylene-7,9-dicarboxylic acid diethyl ester



13

In a 3-necked round-bottomed flask were placed 4.25 g of acenapthaquinone, 5.5 g of diethyl 1,3-acetonedicarboxylate, and 75 mL of methanol. To this suspension 4.5 mL of triethylamine dissolved in 10 mL of methanol was added dropwise. When the addition was completed, the suspension was stirred at 40 °C for 24 hours. The resulting dark suspension was filtered, washed with methanol, and the material that remained was separated over silica gel using methylene chloride as an eluant. Removal of the solvent afforded 2.02 g

Table 1.4.2.1



Compound:		Directory: [USERS.FRONZ.CLAYTON1]
Formula: $C_{27}H_{20}O_3$	FW: 392.5	F_{000}: 824
Space Group: $P2_1/n$	Radiation: CuK_α	Z: 4
a: 14.1355(7)Å	b: 8.2942(3)Å	c: 17.0996(11)Å
α:	β: 106.895(5)°	γ:
V: 1918.3(4)Å^3	D_C: 1.359 gcm^{-3}	D_m:
μ: 6.6 cm^{-1}	T: 25° C	θ Limits: 2-75.7°
R_{int}: 0.011	Max. Transm: 99.99%	Av. Transm: 99.04%
Min. Transm: 97.90%	Xtal Size:0.22x0.20x0.12mm	Color: Yellow fragment
Max. Decay:	Av. Decay:	Min. Decay:
R(obs. data): 0.049	R(all data): 0.064	R_W: 0.055
Unique Data: 3985	Obs Data: 3266	GOF: 2.171 Cutoff: I>1σ(I)
Max. Shift: < 0.01σ	Variables: 272	Fudge: 0.02
Max. Residual: 0.26 eÅ^{-3}	Min. Residual: -0.07 eÅ^{-3}	Extinction: 2.94(12)x10^{-6}

Comments:
Hydrogen atoms not refined.

Table 1.4.2.2 Positional Parameters and Their Estimated Standard Deviations

Atom	x	y	z	B(A2)
O1	0.6592 (1)	0.1406 (2)	0.26345 (8)	4.68 (3)
O2	0.5041 (1)	- 0.1788 (2)	0.03815(9)	4.81 (4)
O3	0.9208 (1)	0.1908 (2)	0.3869 (1)	6.82 (4)
C1	0.8006 (1)	0.1402 (2)	0.5609 (1)	2.86 (3)
C2	0.8934 (1)	0.1864 (2)	0.6062 (1)	3.41 (4)
C3	0.9351 (2)	0.1138 (3)	0.6836 (1)	3.98 (5)
C4	0.8852 (2)	0.0036 (3)	0.7158 (1)	4.07 (5)
C5	0.7265 (2)	-0.1582 (3)	0.6944 (1)	4.24 (5)
C6	0.6370 (2)	-0.2005 (3)	0.6416 (1)	4.30 (5)
C7	0.6035 (1)	-0.1408 (3)	0.5613 (1)	3.67 (4)
C8	0.6601 (1)	-0.0277 (2)	0.5371 (1)	2.93 (4)
C9	0.7510 (1)	0.0214 (2)	0.5929 (1)	2.95 (4)
C10	0.7888 (1)	-0.0463 (2)	0.6710 (1)	3.45 (4)
C11	0.7293 (1)	0.1951 (2)	0.4803 (1)	2.65 (3)
C12	0.6551 (1)	0.0556 (2)	0.4609 (1)	2.78 (3)
C13	0.6148 (1)	0.0318 (2)	0.3796 (1)	2.94 (4)
C14	0.6713 (1)	0.1305 (2)	0.3366 (1)	3.18 (4)
C15	0.7584 (1)	0.2159 (2)	0.4004 (1)	2.88 (4)
C16	0.6695 (1)	0.3472 (2)	0.4975 (1)	3.34 (4)
C17	0.7288 (2)	0.4667 (3)	0.5589 (1)	4.07 (5)
C18	0.8061 (2)	0.5542 (2)	0.5546 (1)	4.32 (5)
C19	0.8624 (2)	0.5573 (3)	0.4961 (1)	4.38 (5)
C20	0.8472 (2)	0.4914 (3)	0.4221 (1)	4.13 (5)
C21	0.7622 (2)	0.3917 (2)	0.3715 (1)	3.56 (4)
C22	0.6655 (2)	0.4717 (2)	0.3663 (1)	4.04 (5)
C23	0.6203 (1)	0.4436 (2)	0.4223 (1)	3.97 (5)
C24	0.5367 (1)	-0.0869 (2)	0.3403 (1)	3.53 (4)
C25	0.4968 (2)	-0.0888 (3)	0.2499 (2)	6.53 (7)
C26	0.8529 (1)	0.1225 (2)	0.4017 (1)	3.64 (4)
C27	0.8585 (2)	-0.0547 (3)	0.4187 (1)	4.52 (5)

Table 1.4.2.3 Coordinates Assigned to Hydrogen Atoms.

Atom	x	y	z	B(A2)

Table 1.4.2.3 cont'd

H2	0.929	0.2655	0.5861	4
H3	1.0002	0.1429	0.7142	5
H4	0.9152	-0.04	0.7685	5
H5	0.7469	-0.2045	0.7474	5
H6	0.596	-0.2731	0.6599	5
H7	0.5431	-0.1776	0.5247	4
H16	0.6224	0.2959	0.519	4
H17	0.7084	0.4814	0.6067	5
H18	0.8285	0.6287	0.5982	5
H19	0.9217	0.6181	0.5137	5
H20	0.8983	0.5105	0.3973	5
H21	0.7734	0.3854	0.3194	4
H22	0.6366	0.543	0.3223	5
H23	0.5556	0.4849	0.415	5
H25a	0.4417	-0.1596	0.234	8
H25b	0.5466	-0.1246	0.2268	8
H25c	0.4765	0.0169	0.2308	8
H27a	0.8168	-0.1107	0.3732	5
H27b	0.8375	-0.0756	0.4657	5

Table 1.4.2.4 Bond Distances in Angstroms.

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
O1	C14	1.216 (2)	C11	C16	1.593 (3)
O2	C24	1.215 (3)	C12	C13	1.355 (2)
O3	C26	1.203 (3)	C13	C14	1.479 (3)
C1	C2	1.370 (2)	C13	C24	1.487 (2)
C1	C9	1.409 (3)	C14	C15	1.558 (2)
C1	C11	1.522 (2)	C15	C21	1.545 (3)
C2	C3	1.417 (3)	C15	C26	1.538 (3)
C3	C4	1.364 (3)	C16	C17	1.509 (3)
C4	C10	1.417 (3)	C16	C23	1.503 (3)
C5	C6	1.368 (3)	C17	C18	1.330 (3)

Table 1.4.2.4 cont'd

C5	C10	1.416 (3)	C18	C19	1.449 (4)
C6	C7	1.406 (3)	C19	C20	1.338 (3)
C7	C8	1.373 (3)	C20	C21	1.508 (3)
C8	C9	1.419 (2)	C21	C22	1.498 (3)
C8	C12	1.458 (3)	C22	C23	1.318 (3)
C9	C10	1.402 (2)	C24	C25	1.483 (3)
C11	C12	1.532 (2)	C26	C27	1.495 (3)
C11	C15	1.547 (3)			

Table 1.4.2.5 Bond Angles in Degrees.

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
C2	C1	C9	18.6 (2)	C14	C13	C24	25.4 (2
C2	C1	C11	34.6 (2)	O1	C14	C13	27.9 (2
C9	C1	C11	06.7 (1)	O1	C14	C15	22.3 (2
C1	C2	C3	18.6 (2)	C13	C14	C15	09.6 (1
C2	C3	C4	22.6 (2)	C11	C15	C14	02.0 (1
C3	C4	C10	20.4 (2)	C11	C15	C21	15.5 (2
C6	C5	C10	20.9 (2)	C11	C15	C26	12.5 (1
C5	C6	C7	22.6 (2)	C14	C15	C26	07.4 (1
C6	C7	C8	18.3 (2)	C14	C15	C17	06.7 (1
C7	C8	C9	19.1 (2)	C21	C15	C23	11.7 (2
C7	C8	C12	35.4 (1)	C11	C16	C23	15.6 (1
C9	C8	C12	05.3 (2)	C11	C16	C18	13.7 (2
C1	C9	C8	13.3 (1)	C17	C16	C19	05.7 (2
C1	C9	C10	23.6 (2)	C16	C17	C20	28.3 (2
C8	C9	C10	23.0 (2)	C17	C18	C21	32.2 (2
C4	C10	C5	28.2 (2)	C18	C19	C20	32.6 (2
C4	C10	C9	16.0 (2)	C19	C20	C21	30.4 (2
C5	C10	C9	15.8 (2)	C15	C21	C20	15.5 (1
C1	C11	C12	01.6 (1)	C15	C21	C22	08.8 (2
C1	C11	C15	23.9 (2)	C20	C21	C22	10.7 (2
C1	C11	C16	08.4 (1)	C21	C22	C23	20.3 (2
C12	C11	C15	03.6 (1)	C16	C23	C22	21.0 (2
C12	C11	C16	05.7 (1)	O2	C24	C13	20.6 (2
C15	C11	C16	11.5 (1)	O2	C24	C25	20.3 (2
C8	C12	C11	08.2 (1)	C13	C24	C25	19.0 (2

Table 1.4.2.5 cont'd

C8	C12	C13	38.2 (2)	O3	C26	C15	20.1 (2
C11	C12	C13	12.8 (2)	O3	C26	C27	20.2 (2
C12	C13	C14	07.7 (1)	C15	C26	C27	19.6 (2
C12	C13	C24	26.5 (2)				

Table 1.4.2.6 Torsion Angles in Degrees.

Atom 1	Atom 2	Atom 3	Atom 4	Angle
C9	C1	C2	C3	-0.48 (0.27)
C11	C1	C2	C3	175.16 (0.19)
C2	C1	C9	C8	-174.04 (0.17)
C2	C1	C9	C10	3.71 (0.28)
C11	C1	C9	C8	9.21 (0.21)
C11	C1	C9	C12	-173.04 (0.17)
C2	C1	C11	C12	165.38 (0.21)
C2	C1	C11	C15	50.09 (0.30)
C2	C1	C11	C16	-83.53 (0.25)
C9	C1	C11	C12	-18.61 (0.18)
C9	C1	C11	C15	-133.90 (0.17)
C9	C1	C11	C16	92.48 (0.17)
C1	C2	C3	C4	-2.17 (0.31)
C2	C3	C4	C10	1.71 (0.32)
C3	C4	C10	C5	-179.89 (0.22)
C3	C4	C10	C9	1.34 (0.29)
C10	C5	C6	C7	2.12 (0.33)
C6	C5	C10	C4	-176.08 (0.21)
C6	C5	C10	C9	2.69 (0.29)
C5	C6	C7	C8	-4.30 (0.32)
C6	C7	C8	C9	1.52 (0.28)
C6	C7	C8	C12	176.08 (0.20)
C7	C8	C9	C1	-178.78 (0.17)
C7	C8	C9	C10	3.46 (0.28)
C12	C8	C9	C1	5.18 (0.21)
C12	C8	C9	C10	-172.58 (0.17)
C7	C8	C12	C11	167.46 (0.21)
C7	C8	C12	C13	-24.02 (0.40)

Table 1.4.2.6 cont'd

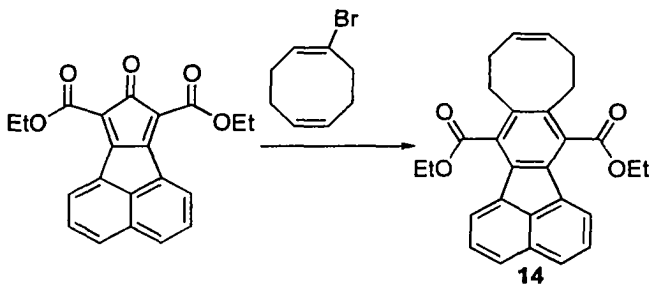
C9	C8	C12	C11	-17.47 (0.19)
C9	C8	C12	C13	151.06 (0.23)
C1	C9	C10	C4	-4.10 (0.28)
C1	C9	C10	C5	176.97 (0.18)
C8	C9	C10	C4	173.43 (0.18)
C8	C9	C10	C5	-5.49 (0.28)
C1	C11	C12	C8	22.17 (0.18)
C1	C11	C12	C13	-149.55 (0.16)
C15	C11	C12	C8	151.62 (0.14)
C15	C11	C12	C13	-20.11 (0.20)
C16	C11	C12	C8	-90.98 (0.16)
C16	C11	C12	C13	97.30 (0.17)
C1	C11	C15	C14	133.86 (0.17)
C1	C11	C15	C21	-110.04 (0.19)
C1	C11	C15	C16	19.87 (0.23)
C12	C11	C15	C14	19.54 (0.17)
C12	C11	C15	C21	135.64 (0.16)
C12	C11	C15	C16	-94.45 (0.17)
C16	C11	C15	C14	-93.73 (0.16)
C16	C11	C15	C21	22.38 (0.21)
C16	C11	C15	C16	152.28 (0.15)
C1	C11	C16	C17	39.74 (0.21)
C1	C11	C16	C23	162.28 (0.16)
C12	C11	C16	C17	148.04 (0.16)
C12	C11	C16	C23	-89.42 (0.18)
C15	C11	C16	C17	-100.01 (0.18)
C15	C11	C16	C23	22.52 (0.21)
C8	C12	C13	C14	-157.44 (0.21)
C8	C12	C13	C24	15.44 (0.36)
C11	C12	C13	C14	10.73 (0.21)
C11	C12	C13	C24	-176.39 (0.17)
C12	C13	C14	O1	178.85 (0.20)
C12	C13	C14	C15	3.13 (0.21)
C12	C13	C24	O2	-2.24 (0.31)
C12	C13	C24	C25	176.10 (0.21)
C14	C13	C24	O2	169.43 (0.19)

Table 1.4.2.6 cont'd

O1	C14	C15	C11	169.17 (0.18)
O1	C14	C15	C21	47.34 (0.24)
O1	C14	C15	C26	-72.63 (0.22)
C13	C14	C15	C11	-14.83 (0.19)
C13	C14	C15	C21	-136.66 (0.16)
C13	C14	C15	C26	103.37 (0.17)
C11	C15	C21	C20	71.58 (0.22)
C11	C15	C21	C22	-53.52 (0.20)
C14	C15	C21	C20	-175.42 (0.16)
C14	C15	C21	C22	59.48 (0.18)
C26	C15	C21	C20	-58.69 (0.21)
C26	C15	C21	C22	176.21 (0.15)
C11	C15	C26	O3	-126.95 (0.19)
C11	C15	C26	C27	55.19 (0.22)
C14	C15	C26	O3	121.99 (0.20)
C14	C15	C26	C27	-55.87 (0.21)
C21	C15	C26	O3	4.85 (0.25)
C21	C15	C26	C27	-173.01 (0.16)
C11	C16	C17	C18	61.87 (0.28)
C23	C16	C17	C18	-64.79 (0.27)
C11	C16	C23	C22	-40.50 (0.26)
C17	C16	C23	C22	87.31 (0.23)
C16	C17	C18	C19	-5.12 (0.40)
C17	C18	C19	C20	11.18 (0.43)
C18	C19	C20	C21	1.93 (0.41)
C19	C20	C21	C15	-74.41 (0.29)
C19	C20	C21	C22	49.72 (0.29)
C15	C21	C22	C23	39.54 (0.25)
C20	C21	C22	C23	-88.34 (0.23)
C21	C22	C23	C16	7.24 (0.30)

of the product in 26% yield: mp 196-198 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.58(d, J = 7.3 Hz, 2H), 8.02(d, J = 8.4 Hz, 2H), 7.71(t, 2H), 4.44(q, 4H), 1.46(t, 6H). ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 192.42, 165.57, 162.28, 146.23, 131.42, 130.73, 129.16, 128.05, 112.20, 61.23, 14.59.

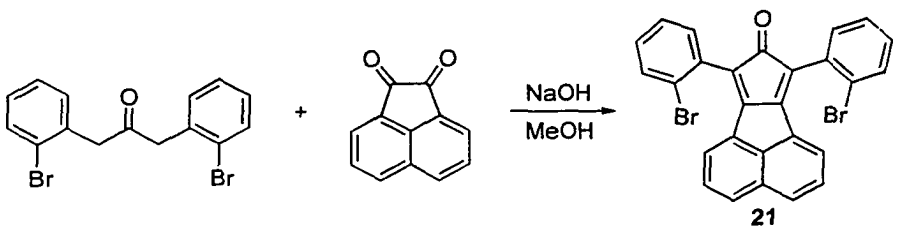
1.4.5 Synthesis of the Octene-ester (14)



14

Bromocyclooctadiene[1.41] (5.2 g) and potassium tert-butoxide were dissolved in 40 mL of dry hexane in a 100 mL round-bottomed flask. In a separate round-bottom flask was dissolved 1.1 g of 18-crown-6 in 40 mL of dry hexane which was promptly transferred to the previous solution via cannula. After refluxing the solution for 1 hour, the suspension that resulted was filtered, diluted with 100 mL of water, washed twice with brine, dried over $MgSO_4$ and filtered into 200 mL of benzene containing 3.2 g of the diethyl-keto-ester (**14**). Evolution of carbon monoxide gas was immediately observed. The solution was then refluxed for 2 hours. After removal of the solvents the crude product was thoroughly washed with hexane to afford 3.4 g of the product in 29% yield: mp187-189 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.84(d, J = 8.31 Hz, 2H), 7.74(d, J = 6.98 Hz, 2H), 7.58(t, 2H), 5.54(t, 2H), 4.59(q, 4H), 3.05(t, 6H), 2.59(q, 4H), 1.47(t, 4H). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 169.62, 136.98, 134.32, 134.28, 133.12, 129.89, 128.79, 127.83, 127.28, 121.77, 61.60, 30.03, 29.11, 14.23. GCMS (m/z, rel. int.) 426(100), 397(14), 381(30), 351(30), 315(24), 307(23), 279(44), 252(41), 239(44), 226(46). Anal. Calcd for $C_{28}H_{26}O_4$: C, 78.85; H, 6.14. Found: C, 78.77; H, 6.11.

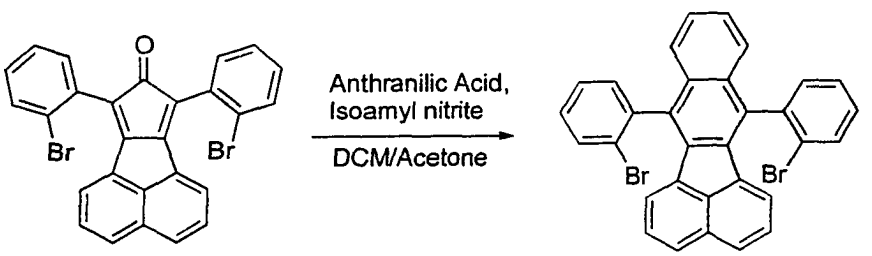
1.4.6 Synthesis 7,9-bis(2-bromophenyl)cyclopenta[*ef*]acenaphthene-8-one



21

To a suspension of 6.16 g of dibenzylketone and 3.05 g of acenapthaquinone in 150 mL of methanol was added 0.640 g of sodium hydroxide. The suspension was allowed to stir at 25 °C for 24 hours. The suspension was then filtered, washed with 100 mL of methanol, and dried to yield 8.28 g (94%) of the dark blue solid: mp 238-239 °C. ^{1}H NMR (250 MHz) δ 7.88 (d, J = 7.2 Hz, 2H), 7.76 (d, J = 8.0 Hz, 2H), 7.44 (m, 10H); ^{13}C NMR (2 rotational isomers), δ 199.65, 155.99, 155.80, 145.28, 133.54, 133.49, 133.02, 132.97, 132.29, 131.95, 131.82, 131.40, 130.01, 128.63, 128.05, 127.41, 124.26, 124.11, 123.44, 123.17, 121.97, 121.79. MS (m/z, rel. int.); 162(100), 324(40), 435(37), 433(37), 326(34), 216(20), 217(19), 514(19). Anal. Calcd for $C_{27}H_{14}Br_2O$: C, 63.07; H, 2.74. Found: C, 62.84; H, 2.65.

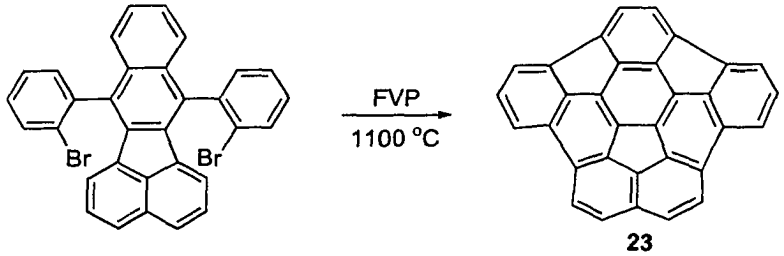
1.4.7 Synthesis of 7,10-bis(2-bromophenyl)benzo[*k*]fluoranthene



22

Isoamyl nitrite, 4.32 mL (32.2 mmol), and compound **21**, 8.28 g (16.1 mmol), were dissolved in 105 mL of dichloromethane and brought to reflux. To this solution was added 4.41 g (32.2 mmol) of anthranilic acid dissolved in 23.7 mL of acetone over a period of two hours. When the addition was complete, the refluxing solution was then allowed to stir overnight. The resultant suspension was then filtered and washed with 25 mL of ethanol to give 5.89 g of yellow solid: mp 300-301 °C. The filtrate was chromatographed on silica gel using cyclohexane/toluene 3:2 respectively to yield another 1.12 g of yellow solid totaling 7.01 g of **22** (83%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (d, J = 7.8 Hz, 2H), 7.75 (d, J = 8.2 Hz, 2H), 7.56 (m, 12H), 6.60 (d, J = 7.1 Hz, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 139.76, 136.52, 135.76, 135.19, 134.06, 133.64, 132.27, 131.97, 130.45, 130.05, 128.51, 128.30, 126.56, 126.42, 124.81, 121.93. MS (m/z, rel. int.) 199(100), 400(31), 562(31). Anal. Calcd for $C_{32}H_{18}Br_2$: C, 68.35; H, 3.23. Found: C, 68.05; H, 3.55.

1.4.8 Flash vacuum pyrolysis of 7,10-bis(2-bromophenyl)benzo-[*k*]fluoranthene

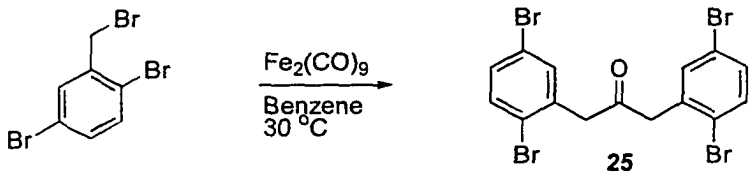


23

Flash vacuum pyrolysis of 5.1 g of 7, 10-bis(2-bromophenyl)-benzo[*k*]fluoranthene at 1100 °C done in 0.20 g portions gave 0.187 g of crude

material after removal of the insoluble material. Chromatography over silica gel using cyclohexane as an eluant and washing with ethanol gave 0.005 g of $C_{32}H_{12}$ as an orange solid: mp softens with increased darkening above 300 °C. ^{1}H NMR (400 MHz, actone-d_6) δ 8.21 (d, J = 9.1 Hz, 2H), 8.11 (d, J = 8.5 Hz, 2H), 7.75 (d, J = 9.1 Hz, 2H), 7.51 (d, J = 7.1, 2H), 7.44 (s, 2H), 7.38 (dd, J = 7.1, 9.1 Hz, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 152.45, 150.34, 149.08, 141.48, 140.92, 140.56, 138.53, 134.18, 133.57, 128.87, 127.50, 126.92, 126.23, 125.85, 123.54, 119.61. HRMS required: 396.0939. Found: 396.0930.

1.4.9 Synthesis of 1,3-di(2, 5-dibromophenyl)propan-2-one

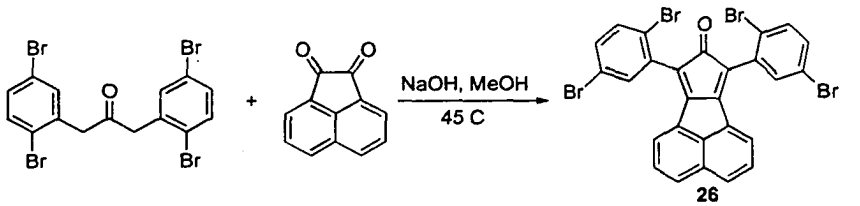


25

2, 5-Dibromobenzylbromide (0.122 mol) and di-ironnonacorbonyl (0.122 mol) were suspended in 152 mL of benzene. The suspension was stirred at 30 °C for 24 hours and then brought to reflux for one hour until a brownish green suspension persisted. The solvent was then evaporated to dryness and 250 mL of dichloromethane was added followed by 150 mL of 10% hydrochloric acid. The two-phase system was stirred at room temperature for a period of 30 minutes in order to dissolve the remaining iron complexes. The organic layer was then separated and the solvent removed. The solid that remained was stirred in 200 mL of ethanol for one hour at room temperature and then filtered to give 27.2 g of white solid in 85% yield: mp 213-214 °C.. Although no further purification of this

material was needed for our purposes, it can be crystalized from toluene. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (d, J = 8.5; 2H), 7.36 (d, J = 2.3 Hz; 2H), 7.28 (dd, J = 2.3, 8.5 Hz; 2H), 3.92 (s, 4H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 201.57, 136.38, 134.80, 134.35, 132.28, 123.90, 121.62, 49.70. MS (m/z, rel. int.) 89(100), 63(62), 249(56), 168(17), 277(10), 447(3), 526.

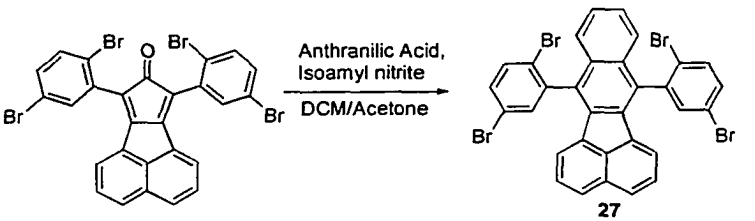
1.4.10 Synthesis of 7,9-bis (2,5-dibromophenyl)cyclopenta[*ef*]acenapthene-8-one



26

To one gram of tetrabromoketone and 0.346 g of acenapthenequinone suspended in 100 mL of methanol was added 0.108 g of sodium hydroxide. The yellow suspension was stirred at 45 °C for 24 hours. The resultant dark suspension was filtered, washed with 50 mL of methanol and dried to yield 1.19 g of **26** (95%): mp 193-194 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (d, J = 7.98 Hz; 2H), 7.60 (m, 8H), 7.42 (dd, J = 2.4, 8.5 Hz; 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 198.4, 156.70, 156.52, 145.38, 134.84, 134.78, 134.67, 134.43, 133.04, 131.95, 130.82, 128.77, 128.56, 123.77, 123.62, 122.92, 122.81, 121.23, 120.51. FAB MS (m/z) 671.7.

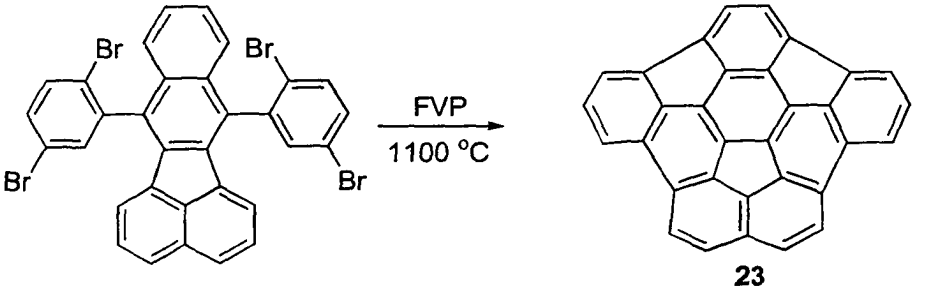
1.4.11 Synthesis of 7,10-bis(2,5-dibromophenyl)benzo[*k*]fluoranthene



27

Anthranilic acid, 2.28 g, was dissolved in 20 mL of acetone. This solution was then added dropwise over a period of two hours to a refluxing solution of 6.9 g of **27** and 2.23 mL of isoamyl nitrite dissolved in 90 mL of dichloromethane. The resultant suspension was stirred overnight at room temperature. It was then filtered and washed with 50 mL of acetone to give 4.75 g of light yellow solid in 64% yield. The compound melted with decomposition between 338-340 °C. ^{1}H NMR (*300 MHz, DMSO-d$_6$*) δ 7.94 (m, 8H), 7.56, (m, 4H), 7.45(m, 2H), 6.59 (d, J = 7.1 Hz; 2H). ^{13}C NMR (75.4 MHz, DMSO-d$_6$) δ 140.42, 135.32, 134.94, 134.52, 134.10, 134.00, 133.66, 132.47, 131.17, 129.96, 128.57, 127.15, 126.98, 125.80, 122.94, 121.79, 131.37. FAB MS (m/z) 719.7.

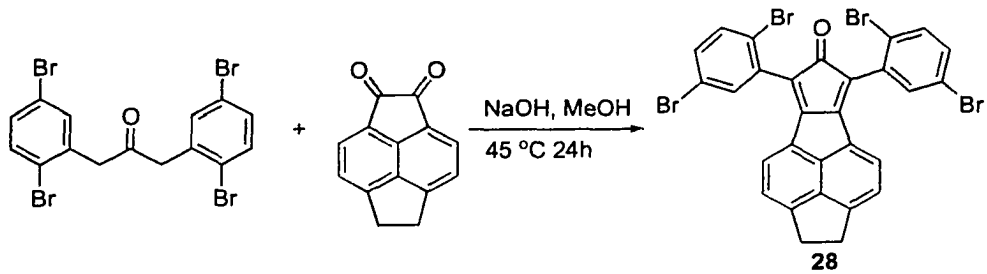
1.4.12 Flash vacuum pyrolysis of 7,10-bis(2,5-dibromophenyl)benzo[*k*]-fluoranthene



23

Flash vacuum pyrolysis of 3.6 g of 7, 10-bis(2,5-dibromophenyl) benzo[*k*]fluoranthene at 1100 °C done in 0.30 g portions gave 0.053 g of crude material after removal of the insoluble material. Chromatography over silica gel impregnated with 2% 2,4,7-trinitro-9-fluorenone using benzene as an eluant gave 0.0034 g of $C_{32}H_{12}$ whose spectral data were identical to those previously reported.

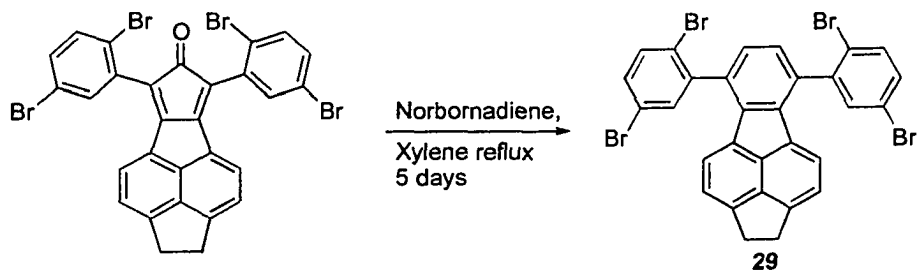
1.4.13 Synthesis of 5,7-bis(2,5-dibromobenzo)-1,2-dihydro-6H-dicyclopent[*a,fg*]acenaphthalen-6-one



28

1,2-Diketopyracene (1.00 g) and 2,5-dibromobenzylketone (2.78 g) were suspended in 75 mL of methanol. To this suspension was added 0.200 g of NaOH and the mixture was stirred at 45 °C for 24 hours. The dark blue suspension that resulted was filtered to give 3.15 g of dark solid in 85% yield: mp 193-194 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.60 (m, 4H), 7.42 (m, 6H), 3.54, (s, 4H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 198.63, 158.80, 148.25, 144.57, 138.61, 134.87, 134.78, 134.52, 132.77, 126.97, 125.50, 122.78, 121.94, 121.13, 119.95, 32.59. FAB MS (m/z) 699.6. Anal. Calcd for $C_{29}H_{14}Br_4O$: C, 49.90; H, 2.02. Found: C, 49.65; H, 1.67.

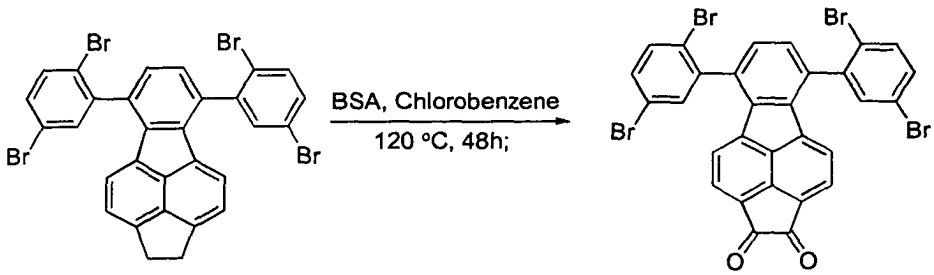
1.4.14 Synthesis of 5,8-bis(2,5-dibromobenzo)-1,2-dihydrocyclopenta[cd]fluoranthene



29

To 450 mL of xylene was added 30.0 g of **28** and 60 mL of norbornadiene. The mixture was refluxed for a period of five days until the violet color of the ketone had disappeared. The solvent was removed to give 22.6 g of the crude product. This material was purified over silica gel using toluene as an eluent to give 13.8 g of a yellow solid in 45% yield. The solid decomposed above 317 °C. ^{1}H NMR (250 MHz, DMSO-d_6) δ 7.88 (d, J = 8.5 Hz, 2H), 7.77 (m, 4H), 7.37(m, 4H), 6.86 (dd, J = 7.1, 2.7 Hz; 2H), 3.45 (s, 4H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 146.84, 143.77, 143.73, 138.19, 136.62, 135.86, 134.64, 134.59, 134.30, 134.07, 132.67, 131.43, 127.79, 124.80, 122.71, 122.68, 121.56, 121.62, 121.20, 32.52. FAB MS (m/z) 695.4.

1.4.15 Synthesis of 5,8-bis(2,5-dibromobenzo)cyclopenta[cd]fluoranthene-1,2-dione

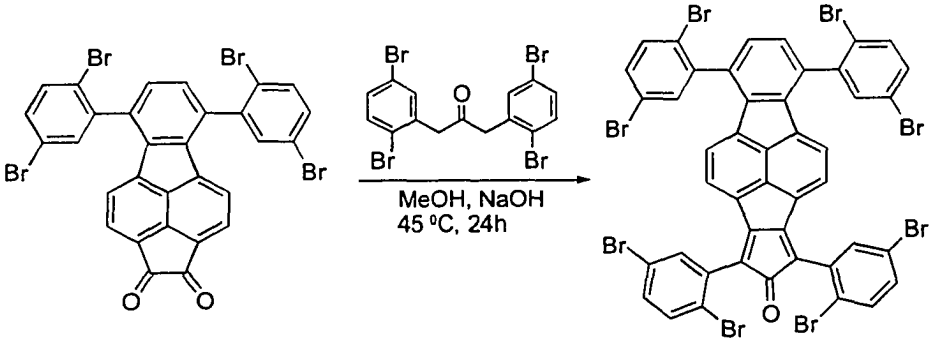


30

5,8-Bis(2,5-dibromobenzo)-1,2-dihydrocyclopenta[*cd*]fluoranthene, 3.0 g, 4.88 g of benzeneseleninic anhydride, and 50 mL of dichlorobenzene were placed in a 100 mL 3-necked flask and heated to 120 °C for a period of 48 hours. The reaction mixture was allowed to cool to room temperature and the solid that precipitated was then filtered and washed with ethanol to yield 2.05 g of a yellow solid. The solvent from the filtrate was removed and the solid that remained was

chromatographed over silica gel using dichloromethane/cyclohexane (3:1) to give an additional 0.362 g for a combined yield of 77%: mp 258-260 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06(dd, J = 3.3, 7.2 Hz; 2H), 7.75 (m, 4H), 7.61 (dd, J = 2.4, 8.5 Hz; 2H), 7.46 (d, J = 2.3; 2H), 7.23 (dd, J = 5.4, 7.2; 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 187.28, 142.09, 142.03, 141.43, 140.47, 138.86, 137.87, 134.95, 134.92, 133.89, 133.67, 133.56, 130.92, 129.89, 128.35, 124.99, 124.51, 122.29, 122.22, 122.04, 122.00. FAB MS (m/z) 724.6. Anal. Calcd for $C_{30}H_{12}Br_4O_2$: C, 49.77; H, 1.67. Found: C, 49.65; H, 1.67.

1.4.16 Synthesis of 1,3,6,9-tetrakis(2,5-dibromophenyl)-2*H*-pentaleno[1,2,3-*cd*]fluoranthen-2-one

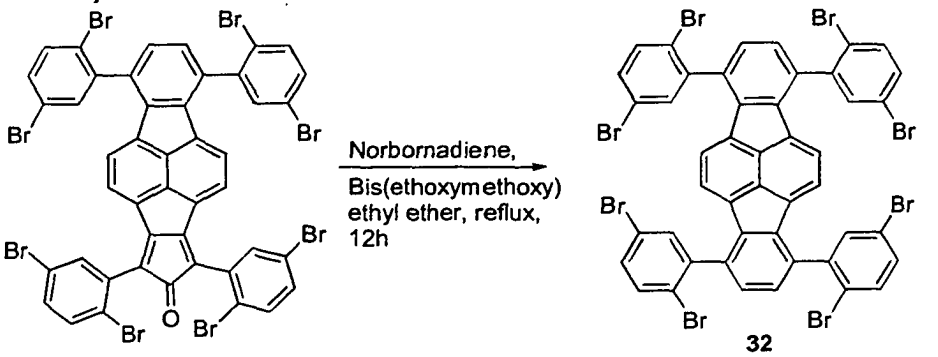


31

In a 3-necked round-bottomed flask equipped with a reflux condenser and a magnetic stirrer were placed 2.48 g of 5,8-bis(2,5-dibromobenzo)-cyclopenta[*cd*]-fluoranthene-1,2-dione, 1.75 g of 2,5-dibromobenzylketone, 0.60 g of sodium hydroxide, and 100 mL of methanol. The reaction mixture was heated to 40 °C for a period of 24 hours. The mixture was then filtered and washed with methanol to yield 2.89 g of the product in 69% yield: mp 282-283 °C. ^{1}H NMR (250 MHz,

$CDCl_3$) δ 7.65(m, 12H), 7.42(m, 4H), 7.18(dd, J = 2.1, 7.5 Hz, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 156.36, 142.74, 142.73, 141.28, 138.31, 137.13, 136.19, 134.81, 134.44, 134.06, 133.83, 133.15, 130.33, 130.01, 129.57, 125.52, 122.75, 122.45, 122.13, 121.82, 121.24. FAB MS (m/z) 1213.9.

1.4.17 Synthesis of 1,4,7,10-tetrakis(2,5-dibromophenyl)-indeno[1,2,3-*cd*]fluoranthene



32

In a 50 mL 3-necked flask equipped with a reflux condenser was placed 2.0 g of **31**, 1.5 mL of norbornadiene, and 20 mL of bis(2-ethoxyethyl)ether. The mixture was refluxed for a period of 12 hours. During this period of time additional portions of norbornadiene were added (3 x 1.0 mL) until the starting material was no longer observed via thin layer chromatography. After the mixture had cooled to room temperature the solid material was filtered and washed with ethanol. This material was then chromatographed over silica gel using toluene/cyclohexane 10:1 to afford 0.540 g of 1,4,7,10-tetrakis(2,5-dibromophenyl)indeno[1,2,3-*cd*]fluoranthene in 27% yield. The compound decomposes above 300 °C. ^1H NMR (300 MHz, DMSO-d_6) δ 7.73(m, 3H), 7.13(m, 1H), 6.34(m, 1H). ^{13}C NMR (75.4 MHz, DMSO-d_6) δ 140.42, 135.32,

134.94, 134.06, 134.00, 133.66, 132.47, 131.17, 128.57, 127.15, 126.98, 125.80, 122.94, 121.79, 121.37. FAB MS (m/z) 1211.7.

1.4.18 Synthesis of 2-bromo-3(prop-3-yne)naphthylene

40

In a 200 mL 3-necked round-bottomed flask were placed 2.0 g of 2-bromo-3-(bromomethyl)napthalene[1.29] and 100 mL of dry tetrahydrofuran. The mixture was cooled to -5 to -10 °C and 14 mL of a 0.6M solution of allenylmagnesium bromide[1.36] was added via cannula. When the addition was complete, the mixture was allowed to warmed to room temperature and stirred for a period of 4 hours. The reaction was then diluted with 30 mL of benzene, thoroughly extracted with water, and dried over $MgSO_4$. After removal of the solvents, 1.7 g of **40** was obtained in 98% yield. The material was used without further purification. ^1H NMR (300 MHz, $CDCl_3$) δ 8.08(s, 1H), 7.76(m, 3H), 7.49(m, 2H), 3.16(t, 2H), 2.66(m, 2H), 2.07(t, 1H). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 136.72, 133.41, 132.49, 131.45, 129.09, 127.61, 126.72, 126.52, 122.66, 83.51, 69.53, 35.38, 19.22. HRMS Calcd for $C_{14}H_{11}Br$: 258.0044, found: 258.0041.

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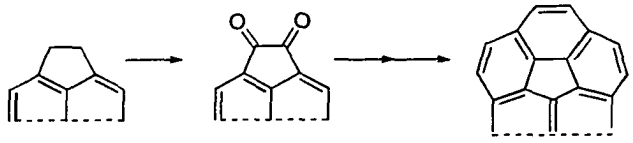
CHAPTER 2 NOVEL TRANSFORMATIONS VIA BENZENESELENINIC ANHYDRIDE OXIDATION

2.1 Introduction

2.1.1 Preface

The first chapter of this dissertation dealt with some advances in fullerene fragment chemistry. This chapter will present a number of examples of different types of oxidations found in the literature employing the use of benzeneseleninic anhydride. In addition, I will discuss how BSA has solved an important synthetic problem that has allowed our group to do further work on fullerene fragments by providing an efficient method for the conversion of benzylic hydrocarbons to 1,2-



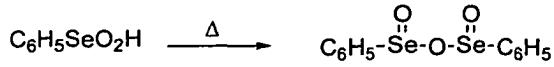
Scheme 2.1.1.1

diketones.(**Scheme 2.1.1.1**) Finally, we will present a novel transformation that has been developed for the conversion of benzylic alkenes to 1,2-diketones using benezeneseleninic anhydride.

2.1.2 Discovery of Benzeneseleninic Anhydride

Among the many reagents available to the synthetic organic chemist, benzeneseleninic anhydride is probably one of the most versatile and yet least known. Howard Doughty first prepared it at the University of Wisconsin in 1909.[2.1] Some years earlier, Doughty was interested in preparing various aromatic

sulpho acids and wanted to investigate the possibility of producing analogous selenium compounds.[2.1] He was successful in producing benzeneseleninic acid via treatment of benzeneselenic acid with hydrochloric acid. When this material was heated in an air bath for 30 hours at 130 °C he obtained a white, quite hygroscopic solid that melted at 164 °C which he deemed benzeneseleninic anhydride (BSA).

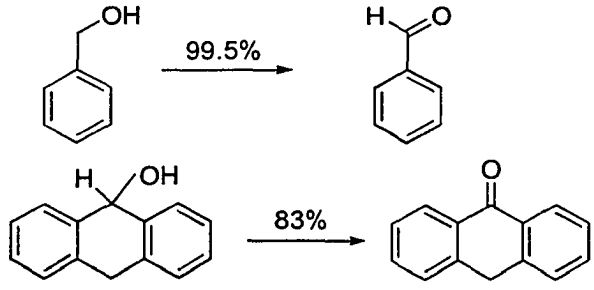


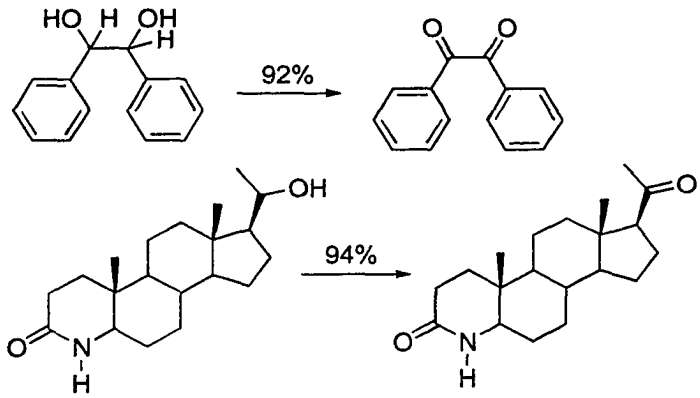
It was not until 1962 that an alternate preparative method was offered by G. Ayrey, D. Barnard , and D. T. Woodbridge.[2.2] They found that BSA could be reliably produced by ozonation of diphenyl diselenide in carbon tetrachloride at −10 °C. This method is still in use today.

2.1.3 Oxidations Employing Benzeneseleninic Anhydride

Since its discovery, BSA has found a variety of uses. It is known for its ability as a dehydrogenating agent as well as its ability to liberate carbonyls from an assortment of protecting groups. For our purposes, its most important application has been as an oxidant.

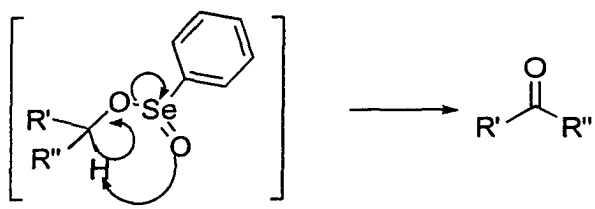
Barton et al. as shown in **Scheme 2.1.3.1** accomplished oxidation of a variety of alcohols to the corresponding ketones via treatment with BSA.[2.3]



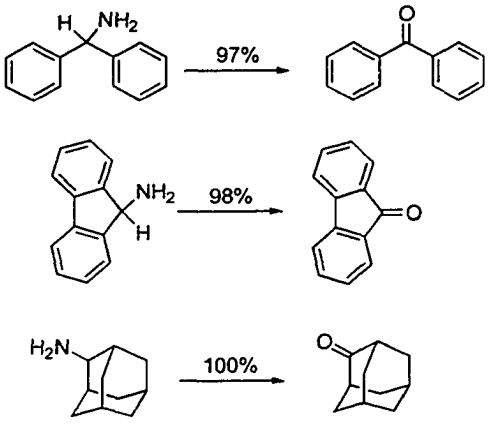


Scheme 2.1.3.1

It was observed that oxidation of benzylic alcohols occurred more rapidly than did allylic or saturated alcohols. The reactions produced only diphenyldiselenide as a by-product, which can be collected and reoxidized to BSA.[2.4] Although mechanistic details are mainly uncharacterized, the ketones produced could only be formed by fragmentation of seleninic esters as shown below.



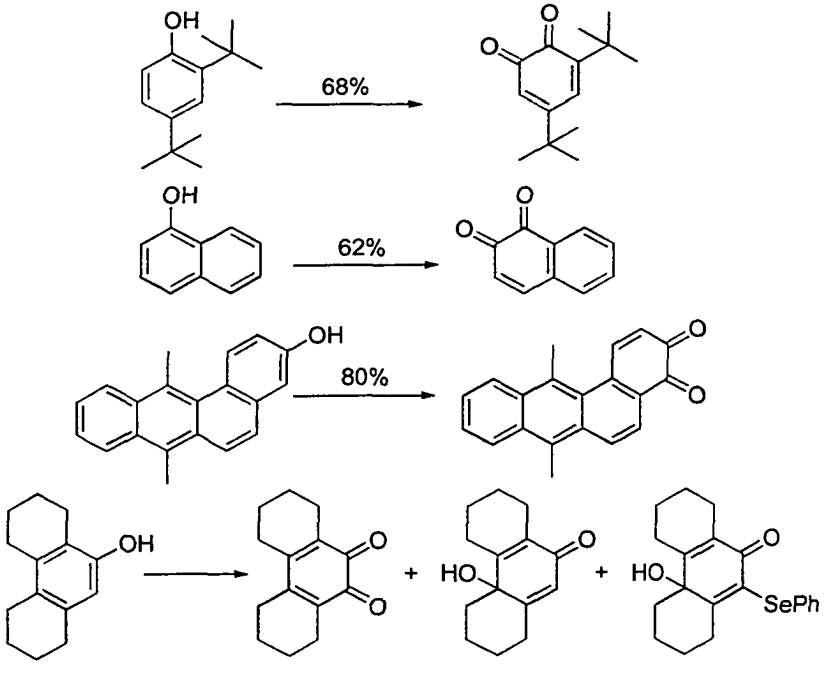
Oxidation of secondary amines to carbonyls using one equivalent of BSA in dichloromethane at room temperature has also been observed. **Scheme 2.1.3.2**[2.5] However, when benzylamine is treated under the same conditions the ketone is not formed and a mixture of benzylic acid and benzonitrile is produced. When treated with 2 equivalents of BSA, benzonitrile is the sole product in 96 % yield.[2.5]



Scheme 2.1.3.2

Phenols can be selectively oxidized to *ortho*-quinones using BSA.[2.6-2.8]

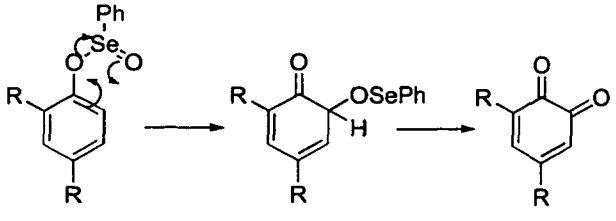
Quinones of this nature usually involve converting 1,2-dihydroxybenzenes into



Scheme 2.1.3.3

such species[2.7] but BSA provides the only direct method from phenols to quinones. Examples of these reactions are given in **Scheme 2.1.3.3**. Formation of these quinones is attributed to the high ortho selectivity of phenolate anion hydroxylation by BSA.

The phenols react to form a selenyl ester, which is followed by a 2,3-sigmatropic rearrangement to give an ortho-selenyl ether. Elimination of phenylselenol then produces the required *ortho*-quinone as shown below.



Having used BSA successfully to effect the oxidation of alcohols, amines, and phenols, Barton et al. further extended the utility of this reagent to incorporate benzylic oxidation as shown in **Table 2.1.3.1**.[2.9]

Table 2.1.3.1

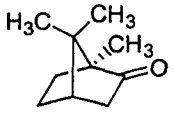
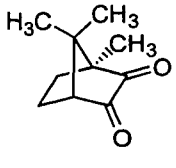
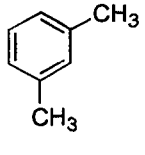
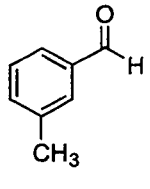
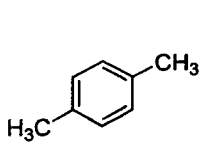
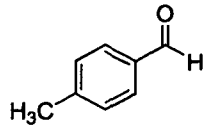
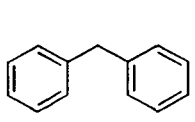
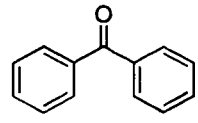
Substrate	Product	Yield (%)	BSA equiv.	Time
		74	—	—
		62	0.33	10 h

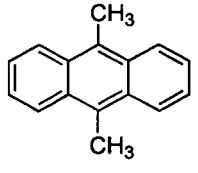
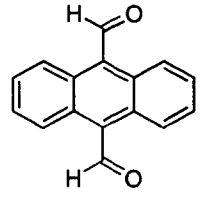
Table 2.1.3.1 cont'd

66 0.33 10 h

90 0.5 4 d

51 1.0 2.5 h

Although it was Barton and co-workers that first observed the tendency of BSA to *ortho*-hydroxylate phenols,[2.10] Yamakawa et al.[2.11-2.12] among others found that this feature could be used to place a hydroxyl group in an angular position on various tricyclic ketones. (**Table 2.1.3.2**)

Table 2.1.3.2

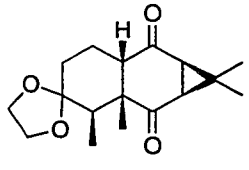
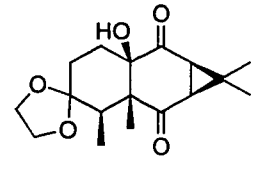
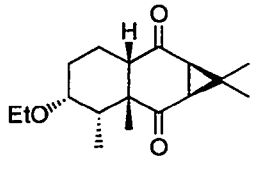
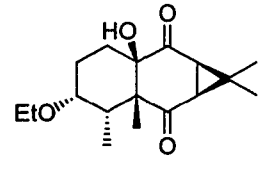
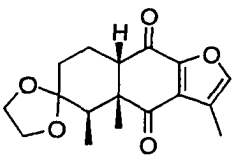
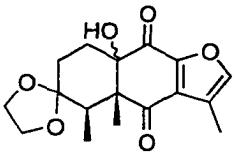
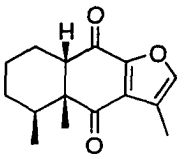
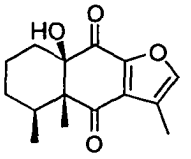
Ketone	Product	Time	Temp.	Solv.	Yield
		4-5 h	110	$PhCH_3$	73%
		4-5 h	110	$PhCH_3$	70%

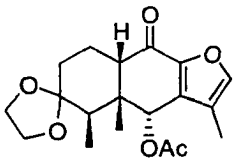
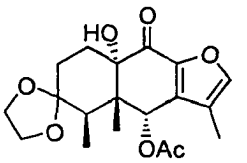
Table 2.1.3.2 cont'd

4 h	110	$PhCH_3$	$\alpha = 17\%$ $\beta = 57\%$

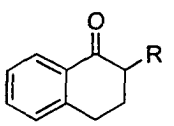
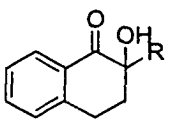
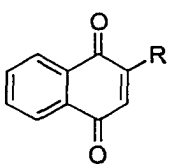
2.5 h	110	$PhCH_3$	42%

2.0 h	131	PhCl	72%

Table 2.1.3.2

They observed that the intermediate selenyl-ester had to be formed in order to place the hydroxyl group in an angular position.[2.12] This was confirmed by alternately treating the phenyl ketones **46** with sodium hydride and aluminum chloride.

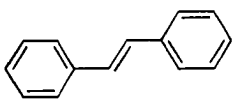
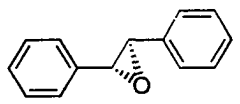
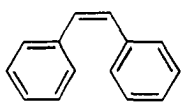
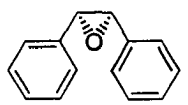
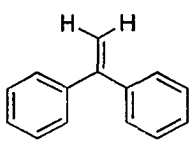
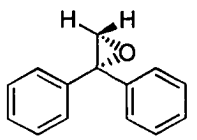
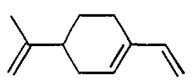
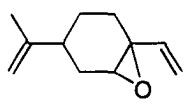
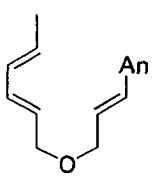
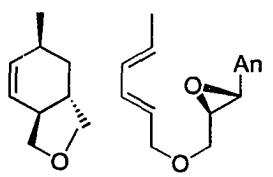
46 **47** **48**

R = Me, Et, or Isopropyl

When 1.1-2.0 equivalents of sodium hydride were added to ensure enolization, the hydroxylated product **47** was produced in 90-94% yield. This result compares to formation of **48** when aluminum chloride was added. When the ketone was treated with BSA alone the quinone was formed in 72-80%.

Benzeneseleninic anhydride has also found some utility in metalloporphyrin-catalyzed epoxidation.[2.13-2.14] Kim and et al. found that when alkenes (**Table 2.1.3.3**) were treated with BSA and catalytic amounts of tris(4-bromophenyl)-aminium hexachloroantimonate in dichloromethane at 0 °C, epoxidation was completed within 10 minutes.[2.15] In addition, the authors note that epoxidation of the stilbenes is completely stereospecific and no *cis/trans* isomerization occurs. Although the mechanism of metalloporphyrin-catalyzed epoxidation is not known in detail, it is thought that the reactions involving BSA are accomplished through a radical cationic process.

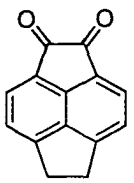
Table 2.1.3.3

Alkene	Epoxide	Yield
		66
		65
		42
		56
		89; 1

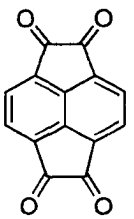
2.2 Results and Discussion

2.2.1 Improvements in the Synthesis of $C_{30}H_{12}$

As discussed in the first chapter, the original methodology in making the first C_{30} was an expansion of Scott et al.'s method for synthesizing corannulene. This procedure required the ability to synthesize gram quantities of the key intermediate **50** from **49**. In fact, the conversion of acenaphthene-type structures to diketones arises as a strategic step in a number of syntheses of fullerene fragments.



49



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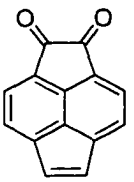
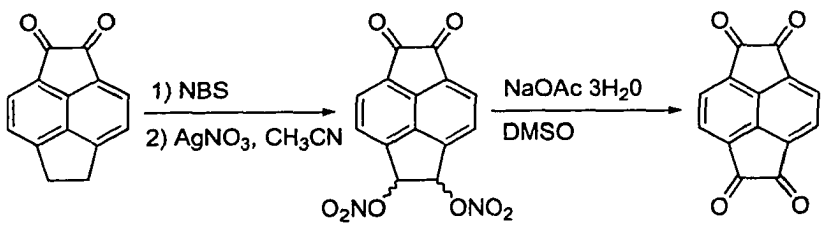


51

Several methods to effect this transformation were attempted unsuccessfully. One example employed the oxidation of **49** using potassium dichromate which resulted in over oxidation to produce the anhydride. Other methods, such as potassium permanganate, chromyl chloride, and palladium dichloride, were used in attempts to oxidize **51** to the target tetraketone but unfortunately they also failed. Some degree of success was accomplished by bromination of **49** with N-bromosuccinimide followed by conversion to the nitrate-ester **52** with silver nitrate in acetonitrile (**Scheme 2.2.1.1**). Oxidation to the tetraketone was accomplished in 55-70% yield by treatment of **52** with a catalytic amount of sodium acetate in dimethylsulfoxide.[2.16] Although this method was

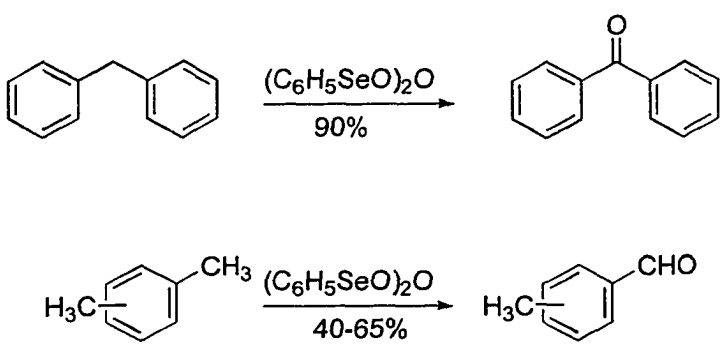
successful in the synthesis of the first semibuckminsterfullerene, it was difficult to reproduce and at times failed altogether. Hence our research program needed a reliable method that would not only give good yields for the conversion of **49** to **50**, but provide a good general method to convert acenapthenes to acenaphthylene quinones.



49 **52** **50**

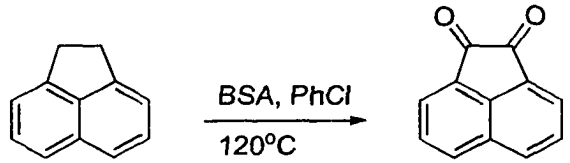
Scheme 2.2.1.1

As noted previously, Barton et al. published a report on benzeneseleninic anhydride's ability to oxidize benzylic hydrocarbons to aldehydes and ketones in good yields.[2.10] **(Scheme 2.2.1.2)** While there was no literature suggesting that this method had ever been used to prepare 1,2-diketones from hydrocarbons, we nonetheless wanted to explore BSA's potential for our systems.



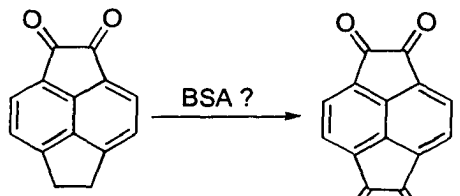
Scheme 2.2.1.2

Acenapthene was selected as a model since it is commercially available as well as structurally similar to **49**. Therefore, acenapthene was treated with two equivalents of benzeneseleninic anhydride in chlorobenzene and heated to 120 °C for 48 hours. After standard workup, followed by chromatography over silica gel, acenapthaquinone (**53**) was produced in 80% yield.



53

While this result showed promise, this had also been the case with many other reagents mentioned previously. The question that needed to be answered was could benzeneseleninic anhydride convert **49** to the required product without over-oxidizing it to the anhydride? This had been the result in all other previous attempts probably due to the additional steric strain introduced by the extra five-membered ring.

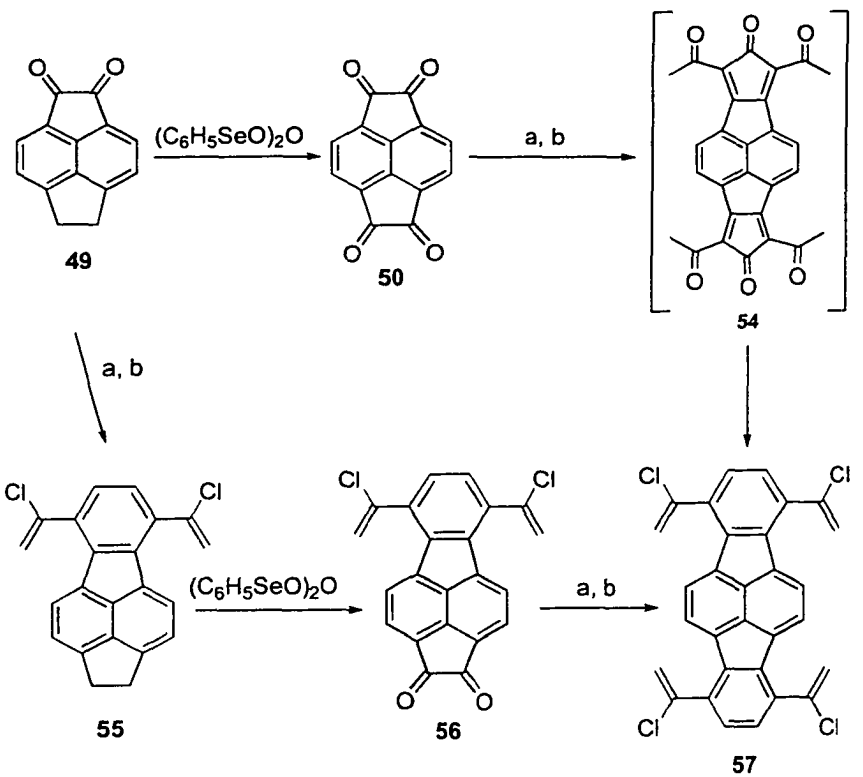


49 **50**

In any event, 1,2-diketopyracene (**49**) was treated with benzeneseleninic anhydride in chlorobenzene for 72 hours to afford the desired 1,2,5,6-tetraketopyracene (**50**) in 82% yield.[2.17] This clearly had proven to be a superior

method as it not only produced the desired product in high yield but also reduced the number of steps from three to one.

Having a good route to **50** was a breakthrough, but it did not solve all of the problems in the synthesis of $C_{30}H_{12}$. In the following step it was known that the yield from the conversion of **50** to **57** was quite low due to the insolubility of intermediate **54**.(**Scheme 2.2.1.3**) It was also known that **55** could be made in good



a. 2,4,6-heptatrione, glycine, norbornadiene, and toluene. b. PCl_5

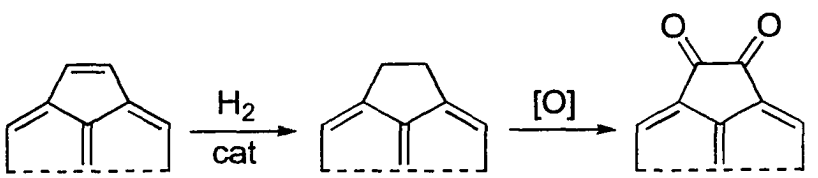
Scheme 2.2.1.3

yield from the starting diketone **49** which represented half of the pyrolytic precursor. If **55** could be oxidized to the diketone **56** using benzeneseleninic

anhydride without harming the chlorovinyl groups, then the solubility of the resultant product would be enhanced, possibly improving the route to the pyrolytic precursor **57**. This indeed turned out to be the case. However, significant losses of material in this alternate route were experienced due to the number of steps being doubled as compared to the original method. Despite this loss of material, the overall yield was improved from 5% in the original method to 10% from this alternate method.[2.17]

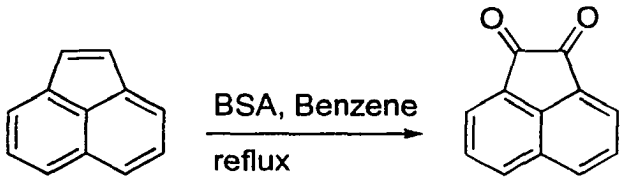
2.2.2 Oxidation of Benzylic Alkenes to 1,2-Diketones

After having been successful in efficiently converting benzylic alkanes to 1,2-diketones, we wondered if it would be possible to effect the same transformation using benzylic alkenes. This transformation would be especially helpful since there are cases where the double bond had to be hydrogenated before oxidation to the diketone.



Since acenapthene served as our model system for the conversion of 1,2-diketopyracene to 1,2,5,6-tetraketopyracene, it seemed logical to use acenapthylene as our test system for this application. When acenapthylene was treated with two equivalents of benzeneseleninic anhydride in benzene for a period of two hours, acenapthaquinone (**53**) was produced in 94% yield. This compares to an 81% yield from acenapthene when done in chlorobenzene at 120 °C over a 24 hour time

period. This result was very interesting for many reasons. The oxidation of the alkene not only gives a near quantitative yield, but is accomplished in only



53

a fraction of the time and at a temperature that is forty degrees lower than when done on the fully saturated acenapthene.

It is not clear why the oxidation of the alkene is much more rapid than the corresponding alkane. It is possible that the increase in the rate of the reaction is due to the higher oxidation state of the benzylic carbons in acenaphthylene as compared to acenapthene. This would reduce the amount of work that the oxidant needs to do to effect the transformation and therefore possibly increase the rate. It is also possible that a major rate-determining step, such as abstraction of the initial proton, had been eliminated.

In Barton et al.'s report of oxidation of various benzylic hydrocarbons to aldehydes and ketones[2.10] there was little discussion as to what mechanisms might be taking place. The presence of diphenyldiselenide as the major side product strongly suggested that the transformation might involve free radical intermediates. This idea is consistent with the fact that reactions of non-benzylic substrates, those that do not have the ability to stabilize radical intermediates, do not yield the corresponding 1,2-diketones.

Using this same logic, one might also argue that this oxidation might occur via cationic processes that could be the result of either protonation or cycloaddition of BSA itself. The former is a possibility since commercially available benzeneseleninic anhydride typically contains between 25-30% benzeneseleninic acid. Perhaps reactions done with pure BSA would resolve this point. However, we decided not to pursue the question as to what the exact mechanistic pathway might be.

After obtaining this result, we tried this oxidant on a variety of systems. The results are summarized in **Table 2.2.2.1**. Oxidation of a series of stilbenes and stilbene-like compounds gave high yields (83-89%) of the corresponding 1,2-diketones. Initially *cis* and *trans* stilbene were oxidized to benzil (**58**) separately to see if conformational orientation might have an effect on either the rate or the yields of oxidation. As there were no significant differences in rate or yield, isomeric mixtures of 1,2-di(2-napthyl)-ethylene[2.19] and 1-(2-napthyl)-2-phenyl-ethylene[2.18] were oxidized to diketones **59** and **60** as shown in sections **2.3.5** and **2.3.6**.

An obvious example was the possible oxidation of 5,6-dihydrocyclopent-[*fg*]acenapthene-1,2-dione[2.20] to 1,2,5,6-tetraketopyracene (**50**), as the oxidation of

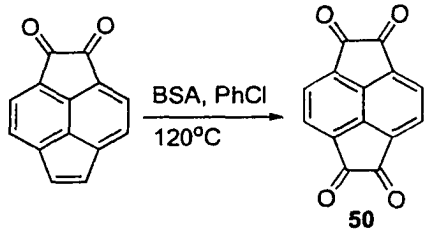


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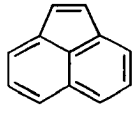
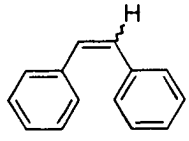
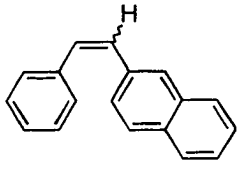
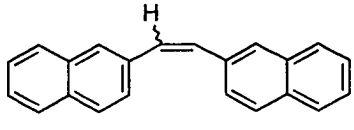
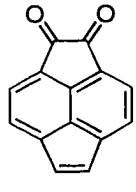
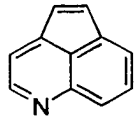
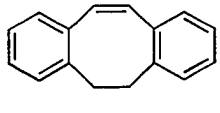
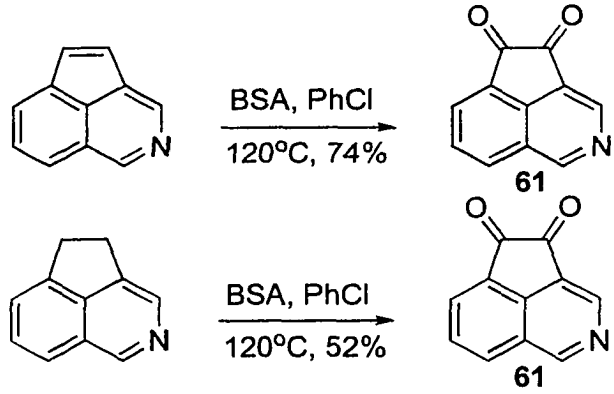
Table 2.2.2.1

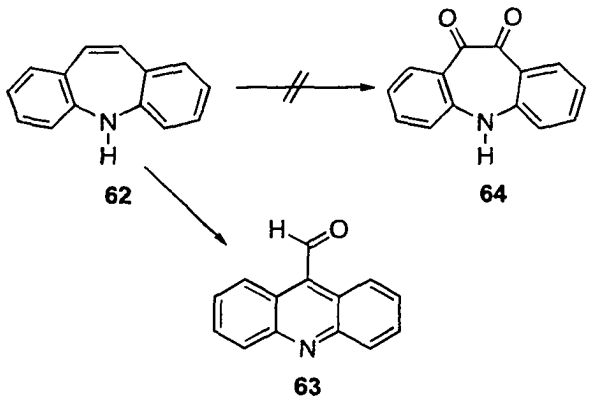
Alkene	Solvent	Temp. (°C)	Time (hrs)	(%) Yield of diketone
	Benzene	reflux	2	94
	PhCl	120	8	89 from cis 82 from trans
	PhCl	120	6	83
	PhCl	120	8.5	86
	PhCl	120	9	52
	PhCl	110	6	74
	PhCl	120	10	25

1,2-diketopyracene had given such marvelous results before. Although the transformation was completed in one eighth of the time, the yield was only 52%. The reaction was then tried in benzene at a lower temperature but the yield did not improve as a result.



Heterocyclic compounds can also be successfully converted to the corresponding 1,2-diketones. 4-Azaacenapthylene was converted into 4-aza-acenapthenquinone (**61**) in 74 % yield over a 6 hour time period.[2.21] This compares favorably with the oxidation 4-aza-acenapthene to 4-aza-acenapthenquinone (**61**) that gave a 52 % yield over a 72-hour time period.[2.21]

In contrast to the smooth oxidation of diarylethylenes and acenaphthylenes, iminostilbene (**62**) was converted to 9-acridinecarboxaldehyde[2.22] (**63**) in 13% yield. ^{1}H NMR in DMSO-d_6 showed a singlet at 11.50, doublets at 8.85 and 8.27, and two triplets at 7.94 and 7.79 ppm, which all integrated for 9 protons. In comparing these data with the published ^{1}H NMR of **64**[2.23] we initially thought that the material we had obtained was the expected diketone (**64**) as the reported



spectrum mentioned only a multiplet between 7.10-7.90 ppm integrating for eight protons and a singlet at 10.85 ppm that integrated for one proton. Since the published spectrum had been taken on a lower field spectrometer, the multiplet could possibly be from (**64**) and the singlet at 11.50 ppm observed in our spectrum might represent the amine proton which might shift with concentration and water content of the deuterated solvent. ^{13}C NMR showed the required four CH carbons but GCMS curiously revealed a mass of 221 amu rather than the required 223 amu. The solution to the puzzle came with an x-ray crystal structure shown in **Figure 2.2.2.1**. The mass at 221 amu seems to represent a minor side product as this compound has a mass of 207 amu. As one can see, the reaction caused the seven-membered ring to contract to a six-membered ring.

The final example listed in **Table 2.2.2.1** is the oxidation of 5,6-dihydrodibenzocyclooctatetraene[2.24] to dibenzo[*a,e*]cyclooctadiene-5,6-dione[2.25] (**65**) in a modest 25% yield. Attempts to improve the yield by lower temperature for longer periods of time with less oxidant were not successful. No evidence of

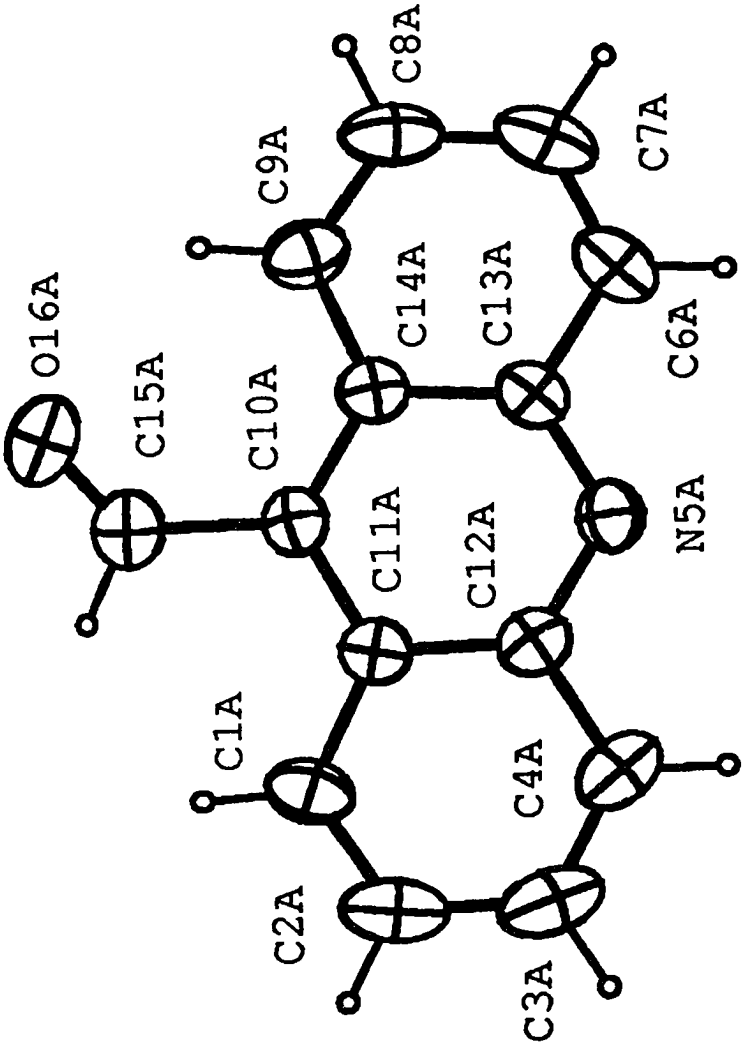
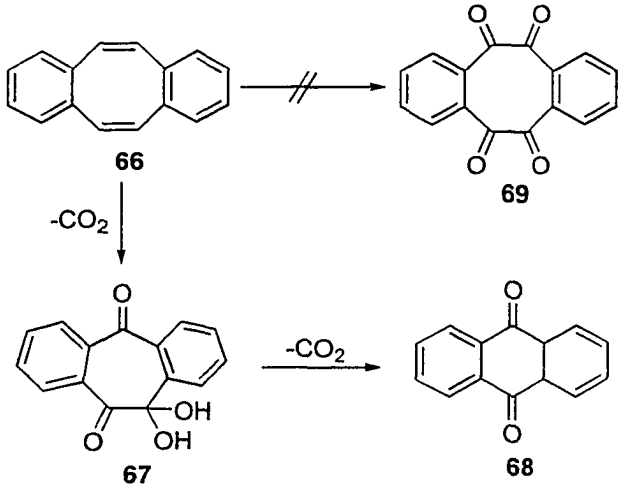


Figure 2.2.2.1

formation of the tetraketone **68** was ever observed even though an excess of BSA was employed.

In an effort to synthesize **69**, dibenzocyclooctatetraene (**66**) as shown in **Scheme 2.2.2.1**, was treated with four equivalents of benzeneseleninic anhydride over a period of 24 hours. After separation over silica gel using 1% ethanol in methylene chloride as an eluant, a small amount of **67** was separated. Slow evaporation of a solution of **67** in chloroform yielded crystals suitable for x-ray crystallography. The results are shown in **Figure 2.2.2.2**. It seems that **66** undergoes a ring contraction followed by loss of one molecule of CO_2 to give **67**. Evidence provided by GCMS showed that small amounts of anthraquinone (**68**)



Scheme 2.2.2.1

were produced via loss of a second molecule of CO_2. These examples show that although benzeneseleninic anhydride is a mild and quite versatile oxidant, its effectiveness may be limited with certain ring systems.

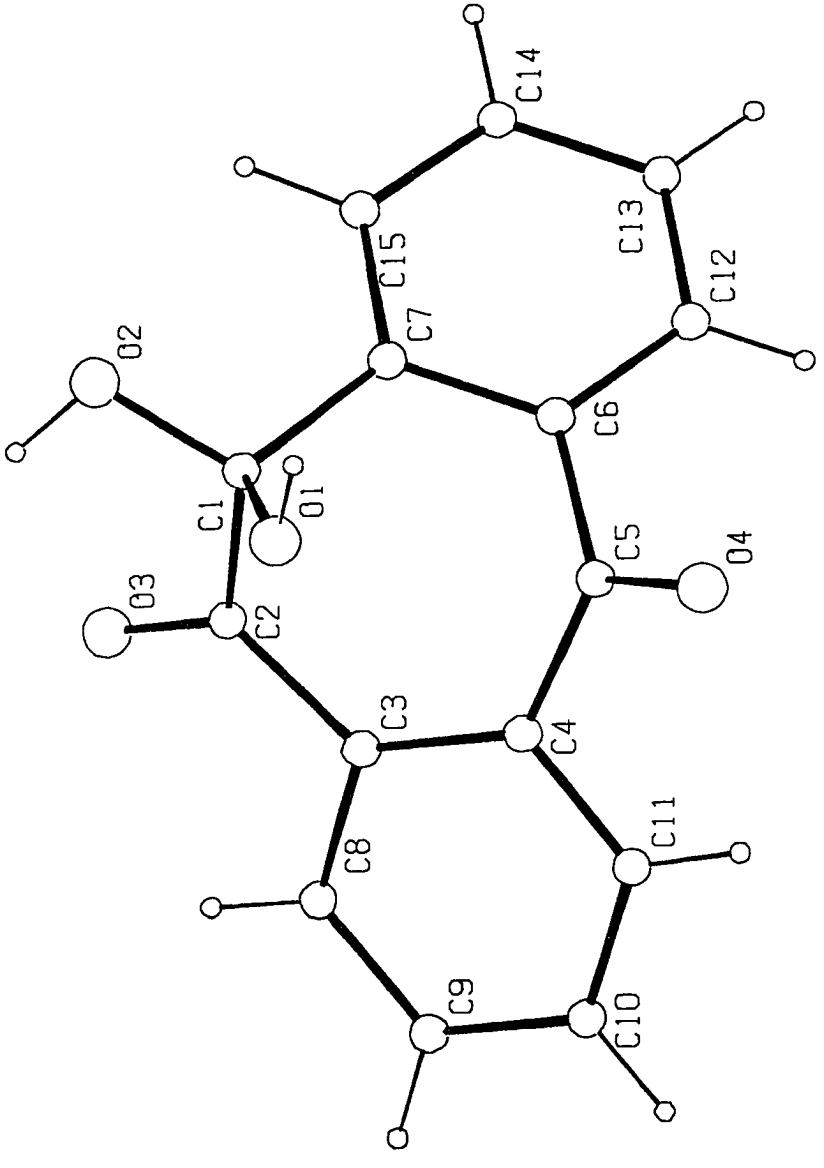
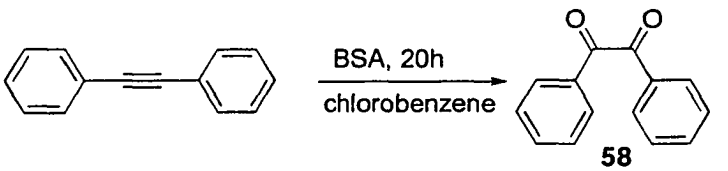


Figure 2.2.2.2

After learning that benzeneseleninic anhydride is a very effective oxidant in converting benzylic single and double bonds to 1,2-diketones, the next logical step was to attempt to convert a benzylic acetylene to a 1,2-diketone. To this end,



58

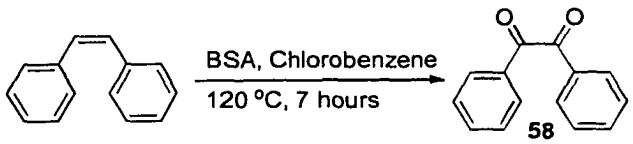
diphenylacetylene was treated with two equivalents of benzeneseleninic anhydride in chlorobenzene for a period of 20 hours. After standard workup followed by chromatography, benzil (**58**) was produced in 86% yield. This result is comparable to the 89 and 82% yields obtained from *cis* and *trans* stilbene respectively. This reaction though roughly equivalent in yield, takes more than twice as long to complete as compared to the stilbenes. This might give some insight into the mechanism. Radical or cationic addition to diarylalkenes give benzylic intermediates which are resonnace stabilized. Similar addition or cycloaddition to diarylacetylenes give vinyl radicals or cations which are less stable.

2.2.3 Conclusions

Benzeneseleninic anhydride is a versatile but mild oxidant that can effect a wide variety of organic transformations ranging from dehydrogenation to carbonyl regeneration. We have shown that it can produce 1,2-diketones from benzylic substrates regardless of the level of unsaturation at the benzylic carbons. The reaction is generally a high yield process in which the products can easily be separated via crystallization or column chromatography.

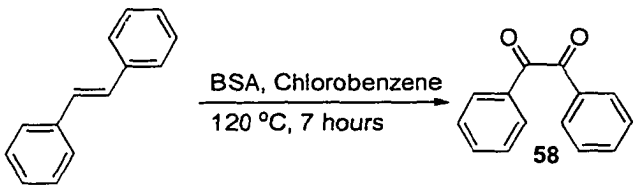
2.3 Experimental

2.3.1 Oxidation of *cis*-Stilbene to Benzil



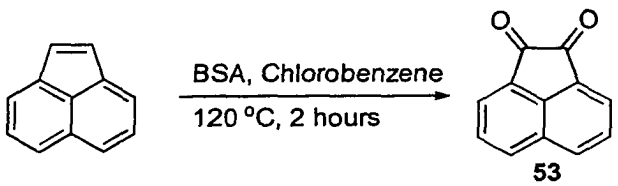
A mixture of 0.05 g of cis-stilbene and 0.286 g of benzeneseleninic anhydride in 10 mL of chlorobenzene was heated to 120 °C for 7 hours. The solution was allowed to cool to room temperature and diluted with 10 mL of dichloromethane. It was then washed three times with 5% $NaHCO_3$ and dried over $MgSO_4$. The solvent was removed and the residue was separated via chromatography over silica using 10% cyclohexane in dichloromethane as an eluant to afford 0.052 g of benzil (**58**) in 89% yield: mp 90 °C (lit.[2.26] mp 91 °C).

2.3.2 Oxidation of *trans*-Stilbene to Benzil



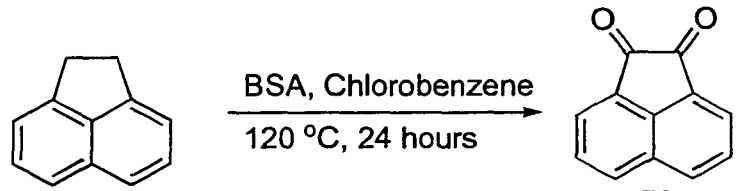
The procedure is exactly the same as for *cis*-stilbene. This method gave 0.048 g of (**58**) (82%): mp 89-90 °C (lit.[2.26] mp 91 °C).

2.3.3 Oxidation of Acenaphthylene to Acenaphthenequinone



A mixture of 0.05 g of 99% acenapthalene and 0.237 g of benzeneseleninic anhydride in 10 ml of chlorobenzene was heated to 120 °C for 2 hours. The solution was cooled to room temperature and the solid that precipitated was filtered and crystallized from a mixture of ethanol and benzene to afford 0.045 g of pure acenapthenequinone. The filtrate and mother liquor were combined and evaporated to dryness. The solid was then separated over silica gel using 10% cyclohexane in dichloromethane to give an additional 0.011g of **53** giving a total yield of 94%: mp 258°C (lit.[2.27] mp 259-260°C).

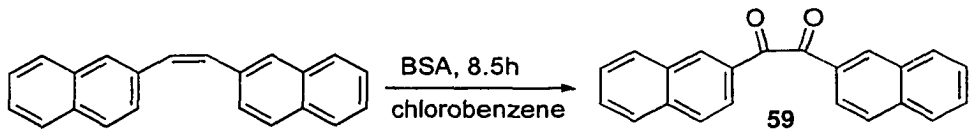
2.3.4 Oxidation of Acenapthene to Acenaphthenequinone



53

A mixture of 0.05 g of acenapthene and 0.334 g of benzeneseleninic anhydride in 10 ml of chlorobenzene was heated to 120 °C for 24 hours. The solution was cooled to room temperature. The solid that precipitated was filtered and crystallized from a mixture of ethanol and benzene to afford 0.038 g of pure acenapthenequinone. The filtrate and mother liquor were combined and evaporated to dryness. The solid was then separated over silica gel using 25% cyclohexane in dichloromethane to give an additional 0.010 g of **53** giving a total yield of 81%: mp 259°C (lit.[2.27] mp 259-260 °C).

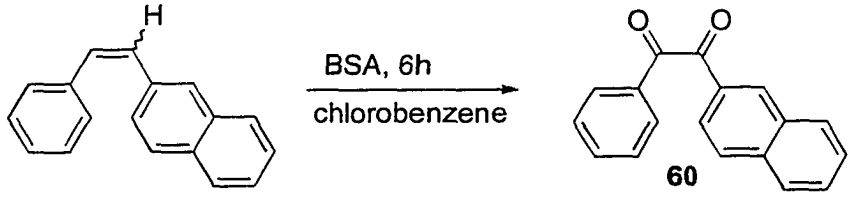
2.3.5 Oxidation of 1,2-di(2-naphthyl)ethylene to di(2-naphthyl)ethanedione



59

To 0.100 g of 1,2-di(2-naphthylene)[2.19] was added 0.386 g of benzene seleninic anhydride and 15 mL of chlorobenzene in a 25 mL 3-necked round-bottomed flask. The mixture was then heated to 120 °C for 8.5 hours. The reaction was allowed to cool to room temperature, diluted with 10 mL of methylene chloride, and washed with a 5% aqueous solution of Na_2CO_3 (3 x 20 mL). The combined aqueous layers were extracted with 5 mL of methylene chloride and this was combined with the organic layer and then dried over $MgSO_4$. After removal of the solvent the residue was chromatographed over silica gel to afford 0.095 g of di(2-napthyl)-ethanedione **59** in 86% yield: mp 157-159 °C (lit. mp[2.28] 157-158 °C). ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.47(s, 2H), 8.17(dd, J = 8.8, 1.9 Hz, 2H), 7.95(m, 6H), 7.64(t, 2H), 7.54(t, 2H). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 194.92, 136.61, 133.82, 132.56, 130.66, 130.15, 129.72, 129.39, 128.15, 127.35, 123.94.

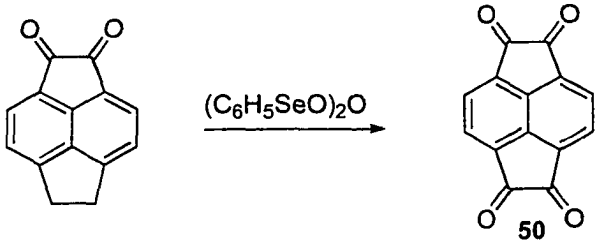
2.3.6 Oxidation of 1-(2-naphthyl)-2-phenylethylene to 1-(napthalen-2-yl)-2-phenylethanedione



60

A mixture of 0.100 g of 1-(2-napthyl)-2-phenylethylene,[2.18] 0.313 g of benzeneseleninic anhydride, and 15 mL of chlorobenzene were heated to 120 °C for a period of 6 hours. The reaction was allowed to cool to room temperature, washed with a 5% aqueous solution of Na_2CO_3, and dried over $MgSO_4$. After removal of the solvent, the residue was chromatographed over silica using cyclohexane/methylene chloride 1:3 as an eluant to give 0.094 g of 1-(napthalen-2-yl)-2-phenylethanedione (**60**) in 83% yield: mp 83-85 °C (lit.[2.29] mp 86.5-87.5 °C). ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.42 (s, 1H), 8.00(m, 6H), 7.60(m, 5H). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 194.86, 136.61, 135.12, 133.76, 133.36, 132.56, 130.54, 130.21, 130.15, 129.75, 129.39, 129.27, 128.78, 127.39, 123.87. GCMS (m/z, rel. int.) 260(5), 155(100), 127(66), 105(24), 77(46), 51(26).

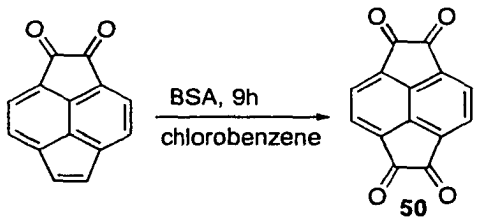
2.3.7 Oxidation of 1,2-diketopyracene to 1,2,5,6-tetraketopyracene



50

A solution of 1,2-diketopyracene (0.832 g) and benzeneseleninic anhydride (2.88 g) in 70 mL of chlorobenzene was heated to 125 °C for 72 hours. After cooling to room temperature the orange precipitate was separated, thoroughly washed with a 5% aqueous solution of $NaHCO_3$, and dried to give 0.770 g of 1,2,5,6-tetraketopyracene (**50**) (82%). This material had identical ^{1}H NMR, ^{13}C NMR, and melting point as compared to literature values.[2.16]

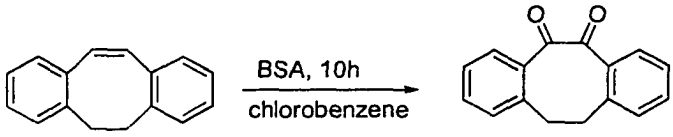
2.3.8 Oxidation of 5,6-dihydrocyclopent[*fg*]acenaphthylene-1,2-dione to 1,2,5,6-tetraketopyracene



50

In a 50 mL round-bottomed 3-necked flask were placed 0.100 g of 5,6-dihydrocyclopent[*fg*]acenaphthylene-1,2-dione,[2.20] 0.414 g of benzeneseleninic anhydride, and 20 mL of chlorobenzene. The mixture was heated to 120 °C for 9 hours. The flask was allowed to cool to room temperature and the solid that precipitated was filtered, and washed with ethyl alcohol to give 0.710 g of 1,2,5,6-tetraketopyracene[2.16] (**50**) in 52% yield. The ^{1}H NMR spectrum taken in DMSO-d_6 shows only a singlet at 8.29 which is identical to the literature value.

2.3.9 Oxidation of dibenzocyclooctatriene to dibenzo[*a,e*]cyclooctadiene-5,6-dione

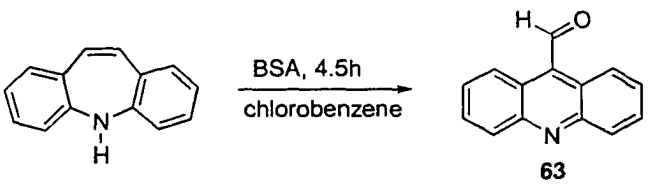


65

In a 25 mL 3-necked round-bottomed flask were placed 0.113 g of dibenzocyclooctatriene,[2.24] 0.768 g of benzeneseleninic anhydride, and 15 mL of chlorobenzene. The mixture was heated to 120 °C for a period of 10 hours. The reaction was allowed to cool to room temperature, washed with a 5% solution of Na_2CO_3 (3 x 10 mL), and dried over $MgSO_4$. After removal of the solvent, the solid was chromatographed over silica gel using methylene chloride/cyclohexane

3:1 as an eluant to afford 0.063 g of dibenzo[*a,e*]cyclooctadiene-5,6-dione[2.25] (**65**) in 25% yield: mp 129-131 °C (lit.[2.25] mp 131-132 °C). The compound may be crystallized from ethanol if necessary. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72(d, J = 7.6 Hz, 2H), 7.47(t, 2H), 7.35(t, 2H), 7.20(d, J = 7.5Hz, 2H), 3.30 (s, 4H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 200.19, 157.31, 142.26, 134.00, 133.48, 130.08, 129.35, 127.45, 34.60. GCMS (m/z, relative intensity) 236(10), 218(10), 207(34), *192(100), 179(75), 165(52), 152(21), 89(86), 76(41), 63(54), 51(56).*

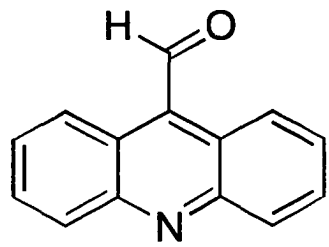
2.3.10 Oxidation of Iminostilbene to 9-acridinecarboxaldehyde



63

In a 3-necked round-bottomed flask fitted with a reflux condenser were placed 0.100 g of iminostilbene, 0.375 g of benzenseleninic anhydride, and 25 mL of chlorobenzene. The mixture was heated to 120 °C for 4.5 hours and then allowed to cooled to room temperature. It was then washed with 10% aqueous solution of Na_2CO_3 (3x 10 mL) and dried over $MgSO_4$. After removal of the solvent the material was separated over silica gel using methylene chloride as an eluant to give 0.033 grams of a yellow solid. The solid was then crystalized from ethyl alcohol to give 0.014 g of **63** as yellow needles in 13% yield: mp 145-146°C (lit.[2.22] mp 147 °C). Crystallographic data are given in **Tables 2.3.10.1-2.3.10.5**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.51(s, 1H), 8.72(d, J = 9.9 Hz, 2H), 8.29(d, J = 8.8 Hz, 2H), 7.82(m, 2H), 7.69(m, 2H). ^{13}C MNR (75.4 MHz, $CDCl_3$) δ 193.83,

Table 2.3.10.1



Compound: 9-Acridinecarboxylate		Directory: [USERS.FRONZ.CLAYTON}
Formula: $C_{14}H_9NO$	FW: 207.23	F_{000}: 864
Space Group: $Pca2_1$	Radiation: CuK_α	Z: 4
a: 7.5192(5) Å	b: 13.247(1) Å	c: 20.124(2) Å
α:	β:	γ:
V: 2004.5(5) $Å^3$	D_c: 1.372 gcm^{-3}	D_m:
μ:	T: 22 °C	θ Limits: 2-70°
R_{int}: 0.000	Max. Transm: 99.82%	Avg. Transm: 94.97%
Min. Transm: 90.12%	Xtal Size: 0.75x0.08x0.07	Color: Yellow needle
Max. Decay:	Avg. Decay:	Min. Decay:
R(obs. Data): 0.043	R(all data):	R_w: 0.046
Unique Data: 1965	Obs. Data: 1895	GOF: 1.988 Cutoff: I>0.0\σ(1)
Max. Shift: <0.01σ	Variables: 240	Fudge: 0.02
Max. Residual: 0.16e$Å^{-3}$	Min. Res: -0.14 e$Å^{-3}$	Extinction: $1.6(7)x10^{-6}$
Comments:		

Table 2.3.10.2 Positional Parameters and Their Estimated Standard Deviations

Atom	X	Y	Z	B (A2)
C1A	0.2602(2)	1.0475(2)	1	0.055(1)
C2A	0.3017(4)	0.9760(2)	1.0450(1)	0.064(2)
C3A	0.2864(4)	0.8726(2)	1.0298(1)	0.075(2)
C4A	0.2294(4)	0.8443(2)	0.9691(1)	0.065(2)
N5A	0.1191(3)	0.8822(1)	0.8619(1)	0.050(1)
C6A	0.0047(3)	0.9113(2)	0.7545(1)	0.058(1)
C7A	-0.0047(3)	0.9737(2)	0.7050(1)	0.060(2)
C8A	-0.0287(4)	1.0779(2)	0.7129(1)	0.063(2)
C9A	0.0335(4)	1.1190(2)	0.7702(1)	0.058(2)
C10A	0.1509(3)	1.0916(2)	0.8857(1)	0.044(1)
C11A	0.1976(3)	1.0218(2)	0.9353(1)	0.043(1)
C12A	0.1804(3)	0.9166(2)	0.9202(1)	0.047(1)
C13A	0.0721(3)	0.9494(2)	0.8153(1)	0.044(1)
C14A	0.0868(3)	1.0567(2)	0.8242(1)	0.043(1)
C15A	0.1755(4)	1.2002(2)	0.8994(1)	0.071(2)
O16A	0.1573(4)	1.2687(1)	0.8652(1)	0.105(2)
C1B	0.2279(4)	0.4487(2)	0.7555(1)	0.051(1)
C2B	0.1749(4)	0.5143(2)	0.8040(1)	0.062(2)
C3B	0.1881(4)	0.6190(2)	0.7945(1)	0.066(2)
C4B	0.2538(4)	0.6564(2)	0.7370(1)	0.060(2)
N5B	0.3801(3)	0.6333(1)	0.6306(1)	0.051(1)
C6B	0.5091(3)	0.6200(2)	0.5238(1)	0.060(1)
C7B	0.5673(3)	0.5646(2)	0.4713(1)	0.063(2)
C8B	0.5579(4)	0.4596(2)	0.4734(1)	0.061(2)
C9B	0.4920(3)	0.4108(2)	0.5279(1)	0.055(1)
C10B	0.3533(3)	0.4216(2)	0.6414(1)	0.043(1)
C11B	0.2973(3)	0.4837(2)	0.6940(1)	0.042(1)
C12B	0.3129(3)	0.5907(2)	0.6854(1)	0.045(1)
C13B	0.4358(3)	0.5733(2)	0.5811(1)	0.045(1)
C14B	0.4264(3)	0.4652(2)	0.5839(1)	0.044(1)
C15B	0.3278(4)	0.3103(2)	0.6476(1)	0.060(2)

Table 2.3.10.3 Coordinates Assigned to Hydrogen Atoms

Atom	X	Y	Z	B(A2)
H1A	0.2729	1.1166	1.0117	0.0738
H2A	0.3421	0.9957	1.0878	0.0929
H3A	0.316	0.8232	1.0622	0.0999
H4A	0.2217	0.7745	0.9588	0.0849
H6A	-0.0064	0.8405	0.7486	0.0778
H7A	-0.0886	0.9468	0.6646	0.0868
H8A	-0.0627	1.1211	0.6774	0.0878
H9A	0.0415	1.1903	0.7742	0.0753
H15A	0.2122	1.2157	0.9434	0.0951
H1B	0.2182	0.3781	0.7631	0.0666
H2B	0.1285	0.4887	0.8446	0.0833
H3B	0.1507	0.6638	0.8287	0.0865
H4B	0.2608	0.7274	0.731	0.0796
H6B	0.5177	0.6915	0.5222	0.0798
H7B	0.6142	0.5975	0.4331	0.0876
H8B	0.581	0.4214	0.4364	0.0845
H9B	0.4897	0.3391	0.5284	0.0731
H15B	0.2715	0.2882	0.6872	0.0787

Table 2.3.10.4 Bond Distances in Angstroms

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
C1A	C2A	1.347(4)	C15A	C2B	1.366(4)
C1A	C11A	1.426(3)	C1B	C11B	1.422(3)
C1A	H1A	0.95	C1B	H1B	0.95
C2A	C3A	1.407(5)	C2B	C3B	1.404(4)
C2A	H2A	0.95	C2B	H2B	0.95
C3A	C4A	1.348(4)	C3B	C4B	1.352(4)
C3A	H3A	0.95	C3B	H3B	0.95
C4A	C12A	1.423(4)	C4B	C12B	1.426(4)
C4A	H4A	0.95	C4B	H4B	0.95
N5A	C12A	1.341(3)	N5B	C12B	1.338(3)

Table 2.3.10.4 cont'd

N5A	C13A	1.340(3)	N5B	C13B	1.342(3)
C6A	C7A	1.344(4)	C6B	C7B	1.360(4)
C6A	C13A	1.418(3)	C6B	C13B	1.419(4)
C6A	H6A	0.95	C6B	H6B	0.95
C7A	C8A	1.394(4)	C7B	C8B	1.394(4)
C7A	H7A	0.95	C7B	H7B	0.95
C8A	C9A	1.357(4)	C8B	C9B	1.365(4)
C8A	H8A	0.95	C8B	H8B	0.95
C9A	C14A	1.424(3)	C9B	C14B	1.426(3)
C9A	H9A	0.95	C9B	H9B	0.95
C10A	C11A	1.405(3)	C10B	C11B	1.404(3)
C10A	C14A	1.405(3)	C10B	C14B	1.406(3)
C10A	C15A	1.476(3)	C10B	C15B	1.492(3)
C11A	C12A	1.432(3)	C11B	C12B	1.433(3)
C13A	C14A	1.437(3)	C13B	C14B	1.434(3)
C15A	O16A	1.147(3)	C15B	O16B	1.164(3)
C15A	H15A	0.95	C15B	H15B	0.95

Table 2.3.10.5 Bond Angles in Degrees

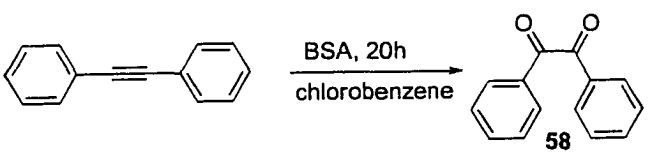
Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
C2A	C1A	C11A	121.5(2)	C2B	C1B	C11B	121.5(2)
C2A	C1A	H1A	119.3	C2B	C1B	H1B	119.3
C11A	C1A	H1A	119.3	C11B	C1B	H1B	119.3
C1A	C2A	C3A	121.3(2)	C1B	C2B	C3B	120.7(2)
C1A	C2A	H2A	119.3	C1B	C2B	H2B	119.6
C3A	C2A	H2A	119.3	C3B	C2B	H2B	119.6
C2A	C3A	C4A	119.5(3)	C2B	C3B	C4B	120.3(3)
C2A	C3A	H3A	120.2	C2B	C3B	H3B	119.9
C4A	C3A	H3A	120.2	C4B	C3B	H3B	119.9
C3A	C4A	C12A	121.5(2)	C3B	C4B	C12B	120.9(2)
C3A	C4A	H4A	119.3	C3B	C4B	H4B	119.5
C12A	C4A	H4A	119.3	C12B	C4B	H4B	119.5
C12A	N5A	C13A	118.5(2)	C12B	N5B	C13B	118.7(2)
C7A	C6A	C13A	121.2(3)	C7B	C6B	C13B	121.4(3)

Table 2.3.10.5 cont'd

C7A	C6A	H6A	119.4	C7B	C6B	H6B	119.3
C13A	C6A	H6A	119.4	C13B	C6B	H6B	119.3
C6A	C7A	C8A	120.2(2)	C6B	C7B	C8B	119.9(3)
C6A	C7A	H7A	119.9	C6B	C7B	H7B	120.1
C8A	C7A	H7A	119.9	C8B	C7B	H7B	120.1
C7A	C8A	C9A	121.5(3)	C7B	C8B	C9B	121.1(3)
C7A	C8A	H8A	119.3	C7B	C8B	H8B	119.5
C9A	C8A	H8A	119.3	C9B	C8B	H8B	119.5
C8A	C9A	C14A	120.9(3)	C8B	C9B	C14B	121.4(2)
C8A	C9A	H9A	119.6	C8B	C9B	H9B	119.3
C14A	C9A	H9A	119.6	C14B	C9B	H9B	119.3
C11A	C10A	C14A	119.6(2)	C11B	C10B	C14B	119.8(2)
C11A	C10A	C15A	118.5(2)	C11B	C10B	C15B	118.5(2)
C14A	C10A	C15A	121.9(2)	C14B	C10B	C15B	121.6(2)
C1A	C11A	C10A	125.1(2)	C1B	C11B	C10B	125.1(2)
C1A	C11A	C12A	117.1(2)	C1B	C11B	C12B	117.2(2)
C10A	C11A	C12A	117.8(2)	C10B	C11B	C12B	117.6(2)
C4A	C12A	N5A	117.8(2)	C4B	C12B	N5B	117.5(2)
C4A	C12A	C11A	119.0(2)	C4B	C12B	C11B	119.4(2)
N5A	C12A	C11A	123.2(2)	N5B	C12B	C11B	123.2(2)
N5A	C13A	C6A	117.5(2)	N5B	C13B	C6B	117.8(2)
N5A	C13A	C14A	123.4(2)	N5B	C13B	C14B	123.2(2)
C6A	C13A	C14A	119.1(2)	C6B	C13B	C14B	119.1(2)
C9A	C14A	C10A	125.3(2)	C9B	C14B	C10B	125.4(2)
C9A	C14A	C13A	117.2(2)	C9B	C14B	C13B	117.2(2)
C10A	C14A	C13A	117.5(2)	C10B	C14B	C13B	117.5(2)
C10A	C15A	O16A	130.0(3)	C10B	C15B	O16B	128.8(3)
C10A	C15A	H15A	115	C10B	C15B	H15B	115.6
O16A	C15A	H15A	115	O16B	C15B	H15B	115.6

154.84, 149.38, 132.54, 130.71, 130.30, 128.98, 123.96, 123.66. GCMS (m/z, rel. int.) 207(77), 179(100), 151(29), 75(24).

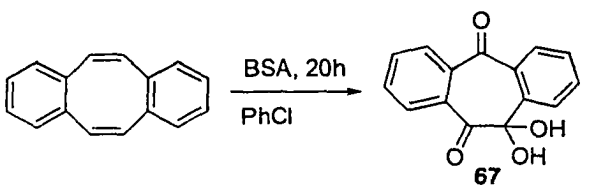
2.3.11 Oxidation of Diphenylacetylene to Benzil



58

In a 25 mL 3-necked round-bottomed flask were placed 0.100 g of diphenylacetylene, 0.404 g of benzeneseleninic anhydride, and 15 mL of chlorobenzene. The mixture was heated to 120 °C for a period of 20 hours. Upon completion, the reaction was allowed to cool to room temperature, diluted with 10 mL of methylene chloride, washed with a 5% aqueous solution of Na_2CO_3 (3 x 10 mL), and dried over $MgSO_4$. After removal of the solvent, the residue was chromatographed over silica gel using cyclohexane/methlyene chloride 3:1 to give 0.102 g of benzil (**58**) in 86% yield: mp 95 °C (lit.[2.26] mp 94-95 °C).

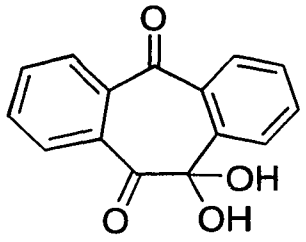
2.3.12 Oxidation of Dibenzocyclooctatetraene to 10,10-dihydroxydibenzo [*a,d*]cyclohepta-5,11-dione



67

In a 25 mL 3-necked round-bottomed flask were placed 0.05 g of dibenzocyclooctatetraene,[2.30] 0.500 g of benzeneseleninic anhydride, and 10 mL of chlorobenzene. The mixture was heated to 120 °C for a period of 20 hours. The reaction was then allowed to cool to room temperature, diluted with 10 mL of methylene chloride, washed with a 5% aqueous solution of Na_2CO_3 (3 x 10 mL), and dried over $MgSO_4$. After removal of the solvent, the residue was chromatographed over silica gel using 1% ethanol in dichloromethane to give 0.035 g of **67**. Crystals for x-ray analysis were grown by slow evaporation of chloroform from the crude fraction. These data are presented in **Tables 2.3.12.1-2.3.12.6.**

Table 2.3.12.1



Compound: Diketonediol		*Directory:* [USERS.FRONZ.CLAYTON}
Formula: $C_{15}H_{10}O_4$	FW: 254.24	F_{000}: 264
Space Group: P_1	Radiation: MoK_α	Z: 4
a: 8.0586(9) Å	b: 8.5313(6) Å	c: 8.9847(7) Å
α: 77.638(6)	β: 70.489(8)	γ: 80.458(7)
V: 565.7(1) $Å^3$	D_c: 1.491 gcm^{-3}	D_m:
μ: 1.02 cm^{-1}	T: 22 °C	θ Limits: 2.5-33°
R_{int}: 0.017	Max. Transm:	Avg. Transm:
Min. Transm:	Xtal Size: 0.40x0.30x0.10mm	Color: Colorless plate
Max. Decay:	Avg. Decay:	Min. Decay:
R(obs. Data): 0.045	R(all data): 0.098	R_w: 0.048
Unique Data: 4252	Obs. Data: 2882	GOF: 1.961 Cutoff: I>0.0\3σ(1)
Max. Shift: <0.01σ	Variables: 212	Fudge: 0.02
Max. Residual: 0.72e$Å^{-3}$	Min. Res: -0.34 e$Å^{-3}$	Extinction:
Comments:		

Table 2.3.12.2 Positional Parameters and Their Estimated Standard Deviations

Atom	X	Y	Z	B(A2)
O1	0.5308(1)	0.27624(9)	0.97030(9)	0.0156(3)
O2	0.2835(1)	0.4667(1)	1.0170(1)	0.0188(3)
O3	0.4494(1)	0.6431(1)	0.7263(1)	0.0211(4)
O4	0.6357(1)	-0.0434(1)	0.7780(1)	0.0179(4)
C1	0.3940(1)	0.3673(1)	0.9114(1)	0.0149(4)
C2	0.4919(1)	0.4692(1)	0.7509(1)	0.0167(4)
C3	0.6404(1)	0.3889(1)	0.6305(1)	0.0161(4)
C4	0.6796(1)	0.2206(1)	0.6349(1)	0.0155(4)
C5	0.5675(1)	0.0943(1)	0.7464(1)	0.0150(4)
C6	0.3708(1)	0.1296(1)	0.7981(1)	0.0144(4)
C7	0.2837(1)	0.2585(1)	0.8782(1)	0.0142(4)
C8	0.7537(2)	0.4915(1)	0.5117(1)	0.0199(5)
C9	0.9018(2)	0.4308(2)	0.3995(1)	0.0209(5)
C10	0.9399(2)	0.2659(2)	0.4033(1)	0.0199(5)
C11	0.8276(2)	0.1627(1)	0.5201(1)	0.0180(5)
C12	0.2740(2)	0.0314(1)	0.7589(1)	0.0172(4)
C13	0.0918(2)	0.0651(1)	0.7960(1)	0.0201(5)
C14	0.0054(1)	0.1910(1)	0.8770(1)	0.0185(5)
C15	0.1001(1)	0.2860(1)	0.9206(1)	0.0166(5)
H1OH	0.485(2)	0.216(2)	1.052(2)	0.031(4)
H2OH	0.334(2)	0.549(2)	0.997(2)	0.055(6)
H8	0.725(2)	0.602(2)	0.513(2)	0.033(4)
H9	0.979(2)	0.503(2)	0.319(2)	0.026(4)
H10	1.043(2)	0.222(2)	0.326(2)	0.029(4)
H11	0.850(2)	0.050(2)	0.522(2)	0.029(4)
H12	0.336(2)	-0.055(2)	0.706(2)	0.026(4)
H13	0.024(2)	0.001(2)	0.767(2)	0.025(4)
H14	-0.123(2)	0.213(2)	0.905(2)	0.025(4)
H15	0.036(2)	0.373(2)	0.981(2)	0.023(4)

Table 2.3.12.3 Coordinates Assigned to Hydrogen Atoms

Atom	X	Y	Z	B(A2)
H1OH	0.485(2)	0.216(2)	1.052(2)	0.031(4)

Table 2.3.12.3 cont'd

H2OH	0.334(2)	0.549(2)	0.997(2)	0.055(6)
H8	0.725(2)	0.602(2)	0.513(2)	0.033(4)
H9	0.979(2)	0.503(2)	0.319(2)	0.026(4)
H10	1.043(2)	0.222(2)	0.326(2)	0.029(4)
H11	0.850(2)	0.050(2)	0.522(2)	0.029(4)
H12	0.336(2)	-0.055(2)	0.706(2)	0.026(4)
H13	0.024(2)	0.001(2)	0.767(2)	0.025(4)
H14	-0.123(2)	0.213(2)	0.905(2)	0.025(4)
H15	0.036(2)	0.373(2)	0.981(2)	0.023(4)

Table 2.3.12.4 Bond distaces in Angstroms

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
O1	C1	1.424(1)	C7	C15	1.391(2)
O1	H1OH	0.81(1)	C8	C9	1.387(2)
O2	C1	1.394(1)	C8	H8	0.94(1)
O2	H2OH	0.82(2)	C9	C10	1.385(2)
O3	C2	1.214(1)	C9	H9	0.96(1)
O4	C5	1.229(1)	C10	C11	1.389(2)
C1	C2	1.546(1)	C10	H10	0.97(1)
C1	C7	1.520(2)	C11	H11	0.95(1)
C2	C3	1.501(1)	C12	C13	1.387(2)
C3	C4	1.413(2)	C12	H12	0.95(1)
C3	C8	1.397(1)	C13	C14	1.384(2)
C4	C5	1.496(1)	C13	H13	0.96(2)
C4	C11	1.389(1)	C14	C15	1.391(2)
C5	C6	1.493(2)	C14	H14	0.98(1)
C6	C7	1.401(2)	C15	H15	0.99(1)

Table 2.3.12.5 Bond Angles in Degrees

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
C1	O1	H1OH	107(1)	C6	C7	C15	119.3(1)
C1	O2	H2OH	105(1)	C3	C8	C9	121.2(1)
O1	C1	O2	111.8(1)	C3	C8	H8	116.5(7)
O1	C1	C2	104.85(8)	C9	C8	H8	122.3(7)
O1	C1	C7	111.53(9)	C8	C9	C10	120.2(1)

Table 2.3.12.5 cont'd

O2	C1	C2	110.55(9)	C8	C9	H9	120.2(8)
C2	C1	C7	109.40(9)	C10	C9	H9	119.6(8)
O2	C1	C7	108.6(1)	C9	C10	C11	119.2(1)
O3	C2	C1	119.2(9)	C9	C10	H10	121.2(8)
O3	C2	C3	121.37(9)	C11	C10	H10	119.6(8)
C1	C2	C3	119.41(9)	C4	C11	C10	121.7(1)
C2	C3	C4	125.37(9)	C4	C11	H11	118.4(7)
C2	C3	C8	115.9(1)	C10	C11	H11	120.0(7)
C4	C3	C8	118.63(9)	C6	C12	C13	119.8(1)
C3	C4	C5	125.81(9)	C6	C12	H12	119(1)
C3	C4	C11	119.12(9)	C13	C12	H12	122(1)
C5	C4	C11	114.9(1)	C12	C13	C14	120.0(1)
O4	C5	C4	119.77(9)	C12	C13	H13	120.6(7)
O4	C5	C6	120.1(1)	C14	C13	H13	1193(7)
C4	C5	C6	119.45(9)	C13	C14	C15	120.5(1)
C5	C6	C7	122.4(1)	C13	C14	H14	119.8(9)
C5	C6	C12	117.4(1)	C15	C14	H14	119.7(9)
C7	C6	C12	120.1(1)	C7	C15	C14	120.1(1)
C1	C7	C6	118.7(1)	C7	C15	H15	120.4(9)
C1	C7	C15	122.0(1)	C14	C15	H15	119.5(9)

Table 2.3.12.6 Torsion Angles in Degrees

Atom 1	Atom 2	Atom 3	Atom 4	Angle
H1OH	O1	C1	O2	64(1)
H1OH	O1	C1	C2	-175(1)
H1OH	O1	C1	C7	-58(1)
H2OH	O2	C1	O1	83(1)
H2OH	O2	C1	C2	-32(1)
H2OH	O2	C1	C7	-152(1)
O1	C1	C2	O3	-129.7(1)
O1	C1	C2	C3	48.9(1)
O2	C1	C2	O3	-9.0(2)
O2	C1	C2	C3	169.5(1)
C7	C1	C2	O3	111.0(1)
C7	C1	C2	C3	-70.5(1)

Table 2.3.12.6 cont'd

O1	C1	C7	C6	-44.5(1)
O1	C1	C7	C15	137.4(1)
O2	C1	C7	C6	-168.78(9)
O2	C1	C7	C15	13.2(1)
C2	C1	C7	C6	70.5(1)
C2	C1	C7	C15	-107.6(1)
O3	C2	C3	C4	-168.3(1)
O3	C2	C3	C8	16.0(2)
C1	C2	C3	C4	13.2(2)
C1	C2	C3	C8	-162.5(1)
C2	C3	C4	C5	8.6(2)
C2	C3	C4	C11	-176.4(2)
C8	C3	C4	C5	-175.8(1)
C8	C3	C4	C11	-0.8(2)
C2	C3	C8	C9	176.1(1)
C4	C3	C8	C9	0.1(2)
C3	C4	C5	O4	-155.8(1)
C3	C4	C5	C6	33.6(2)
C11	C4	C5	O4	29.0(2)
C11	C4	C5	C6	-141.6(1)
C3	C4	C11	C10	1.4(2)
C5	C4	C11	C10	176.9(1)
O4	C5	C6	C7	130.8(1)
O4	C5	C6	C12	-51.8(1)
C4	C5	C6	C7	-58.6(1)
C4	C5	C6	C12	119.6(1)
C5	C6	C7	C1	0.8(2)
C5	C6	C7	C15	178.9(1)
C12	C6	C7	C1	-177.3(1)
C12	C6	C7	C15	0.8(2)
C5	C6	C12	C13	-175.9(1)
C7	C6	C12	C13	2.4(2)
C1	C7	C15	C14	175.0(1)
C6	C7	C15	C14	-3.0(2)
C3	C8	C9	C10	0.2(2)
C8	C9	C10	C11	0.3(2)
C9	C10	C11	C4	-1.1(2)

Table 2.3.12.6 cont'd

C6	C12	C13	C14	-3.2(2)
C12	C13	C14	C15	1.0(2)
C13	C14	C15	C7	2.2(2)

^{1}H NMR ($CDCl_3$, 250 MHz) δ 8.21(dd, J = 1.78, 7.72 Hz, 1H), 8.09, (dd, J = 1.55, 7.70 Hz, 1H), 7.87(d, J = 7.82 Hz, 1H), 7.71(m, 5H), 4.67(s, 2H).

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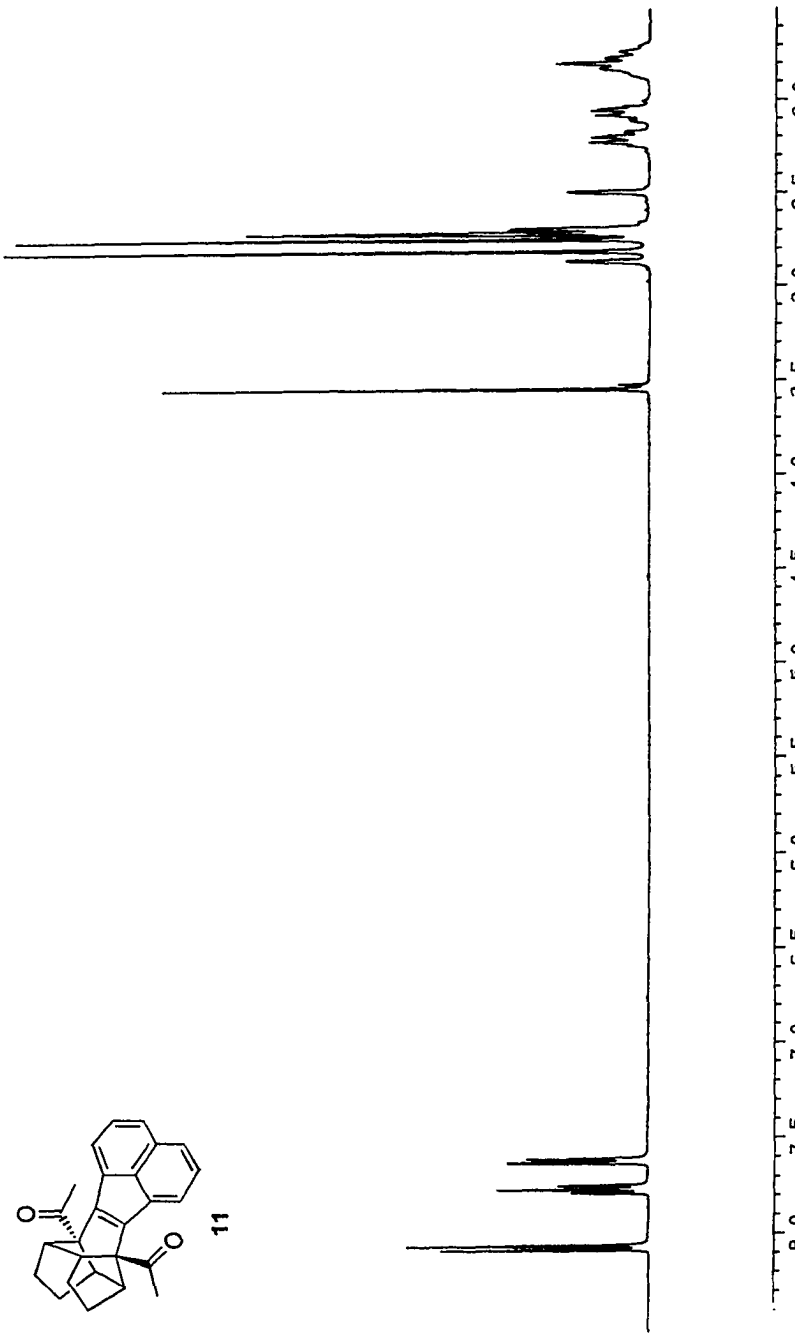
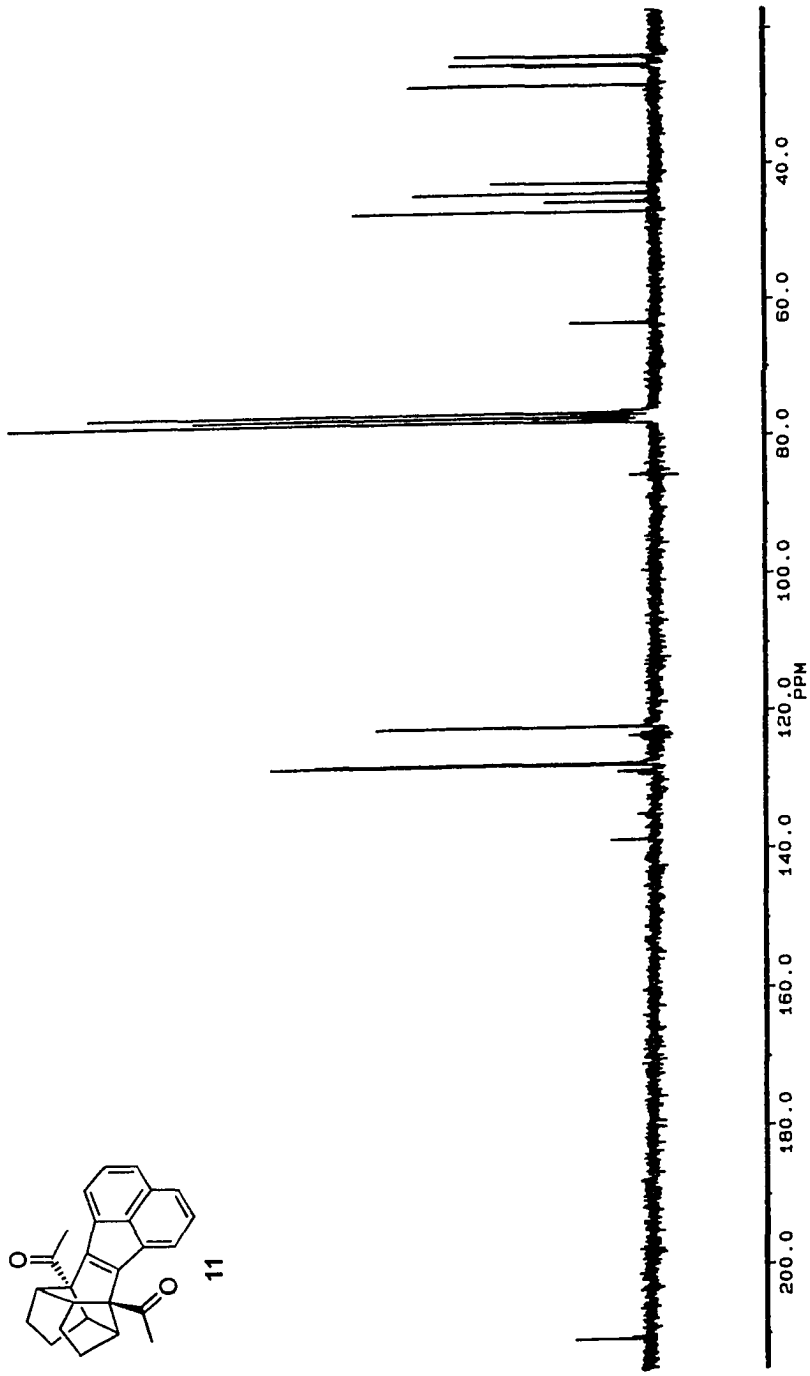
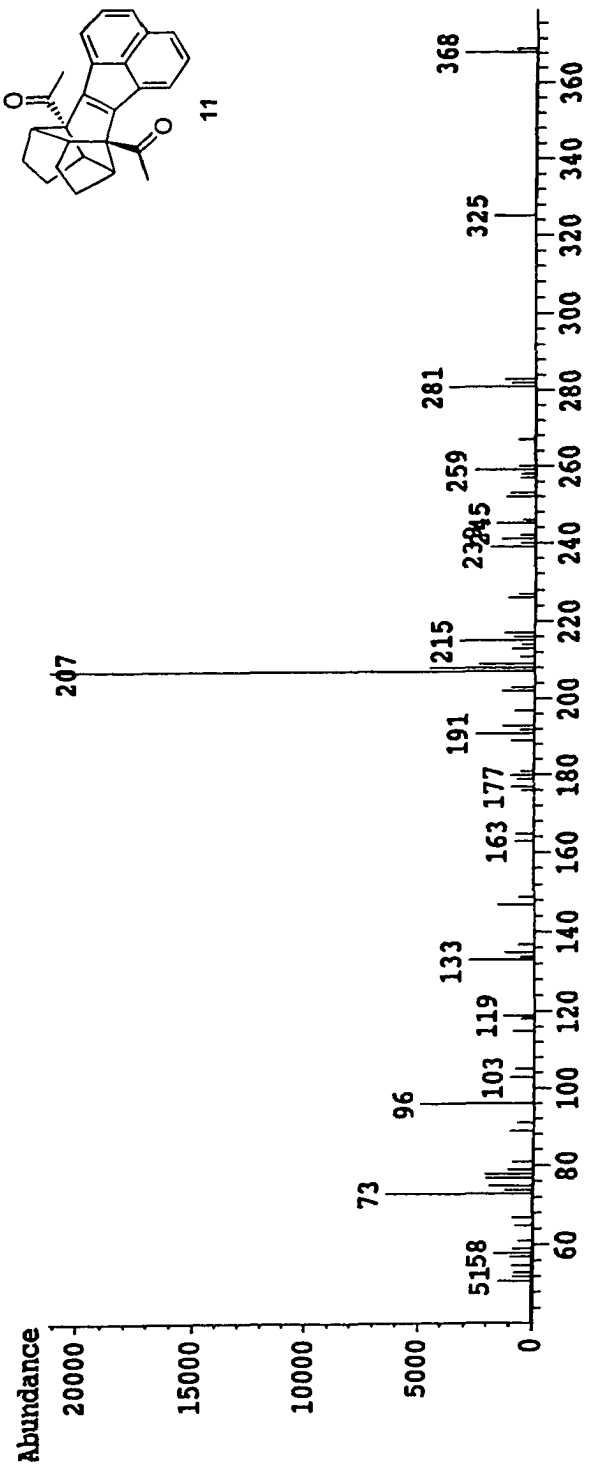
SPECTRAL APPENDIX



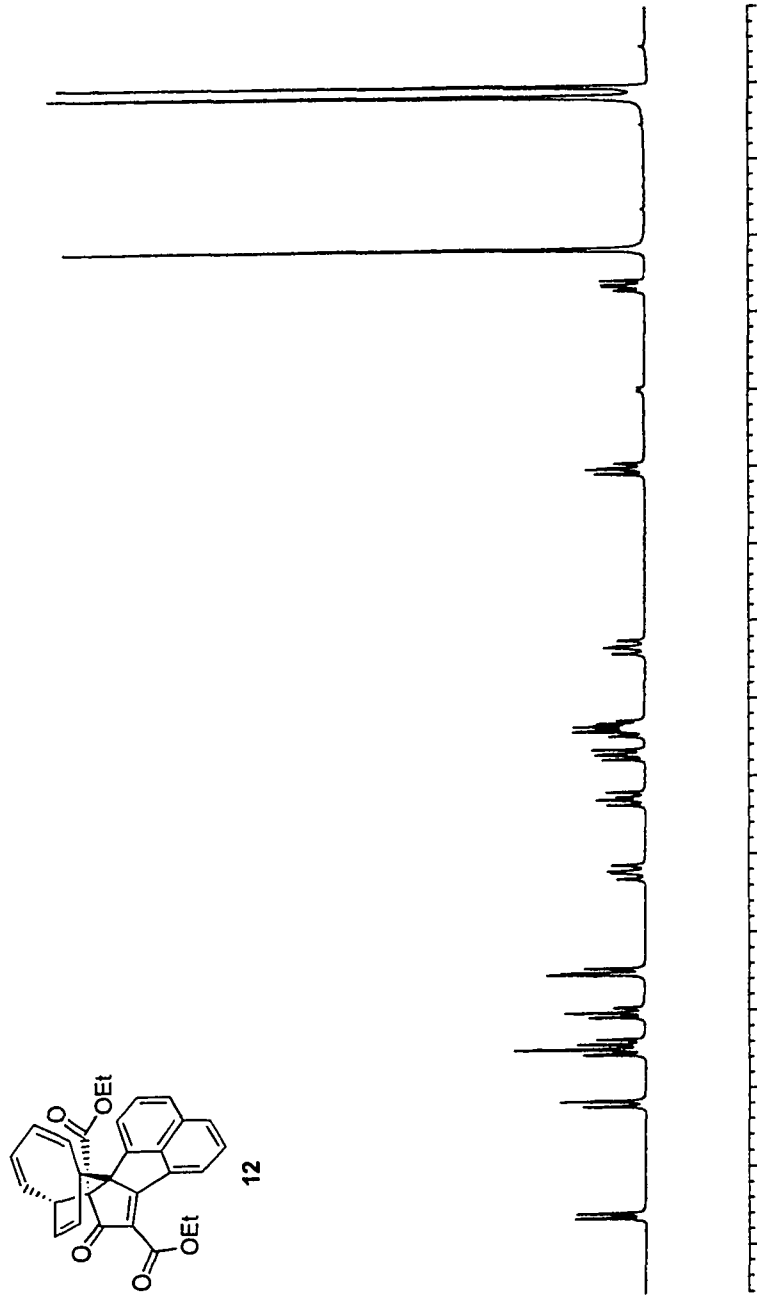
Appendix 1 400 MHz ^{1}H NMR Spectrum of 5,11c-diacetyl-2,3,3a,4,5,11c-hexahydro-4,1,5-[1]propanyl[3]ylidene-1*H*-cyclopenta[*j*]fluoranthene done in DMSO-d_6.



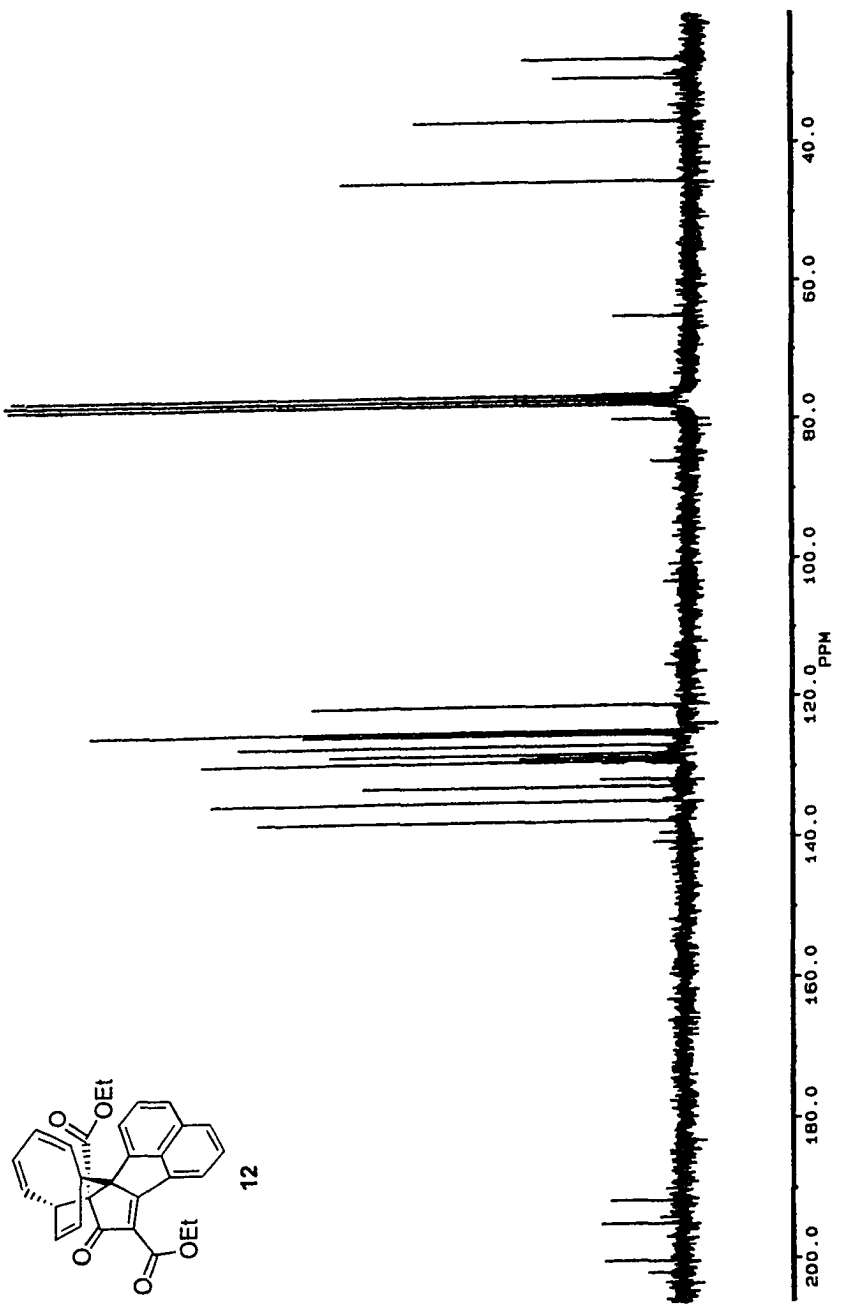
Appendix 2 62.9 MHz ^{13}C NMR Spectrum of 5,11c-diacetyl-2,3,3a,4,5,11c-hexahydro-4,1,5-[1]propanyl[3]ylidene-1*H*-cyclopenta[*j*]fluoranthene.



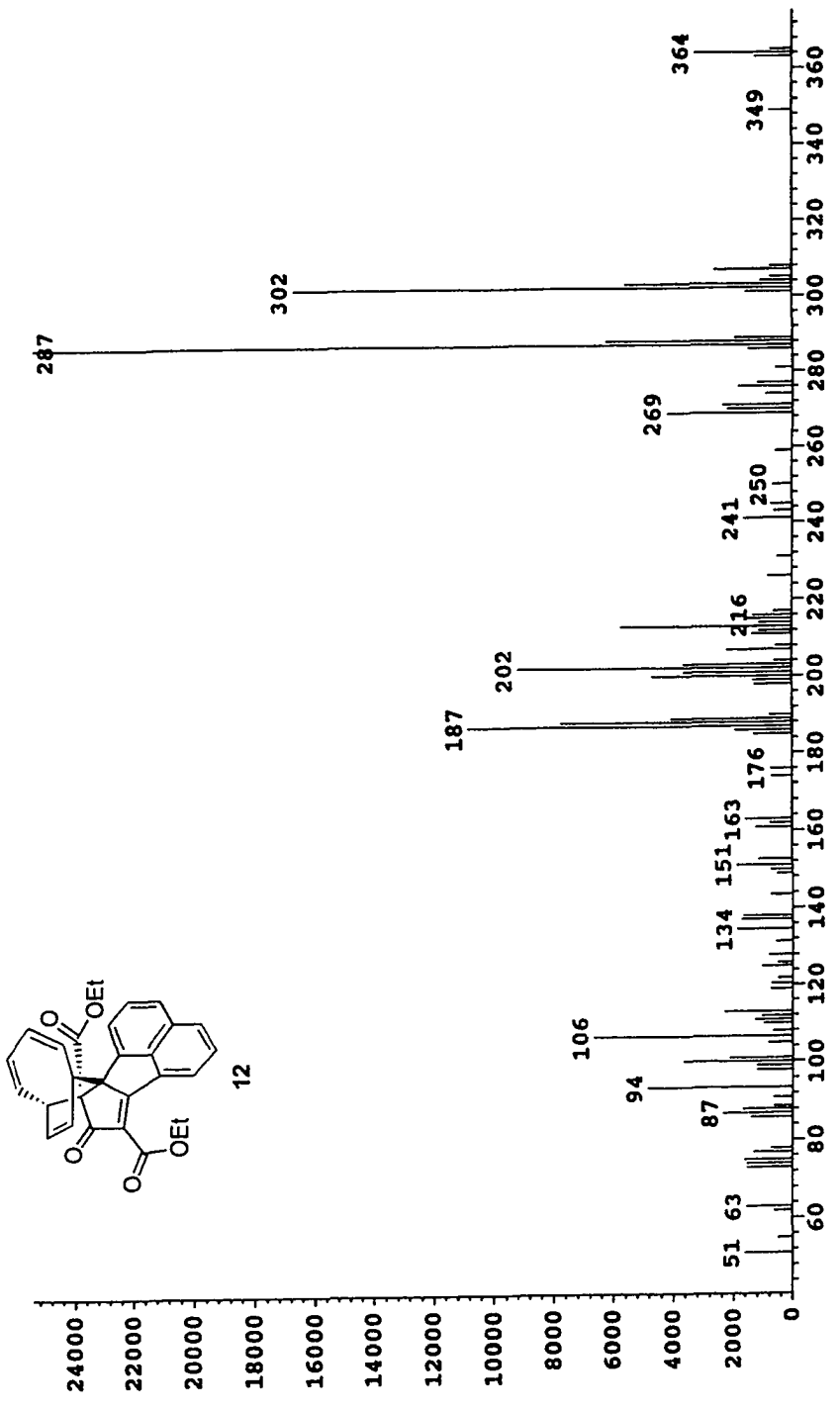
Appendix 3 Mass Spectrum of 5,11c-diacetyl-2,3,3a,4,5,11c-hexahydro-4,1,5-[1]propanyl[3]ylidene-1*H*-cyclopenta[*j*]fluoranthene.



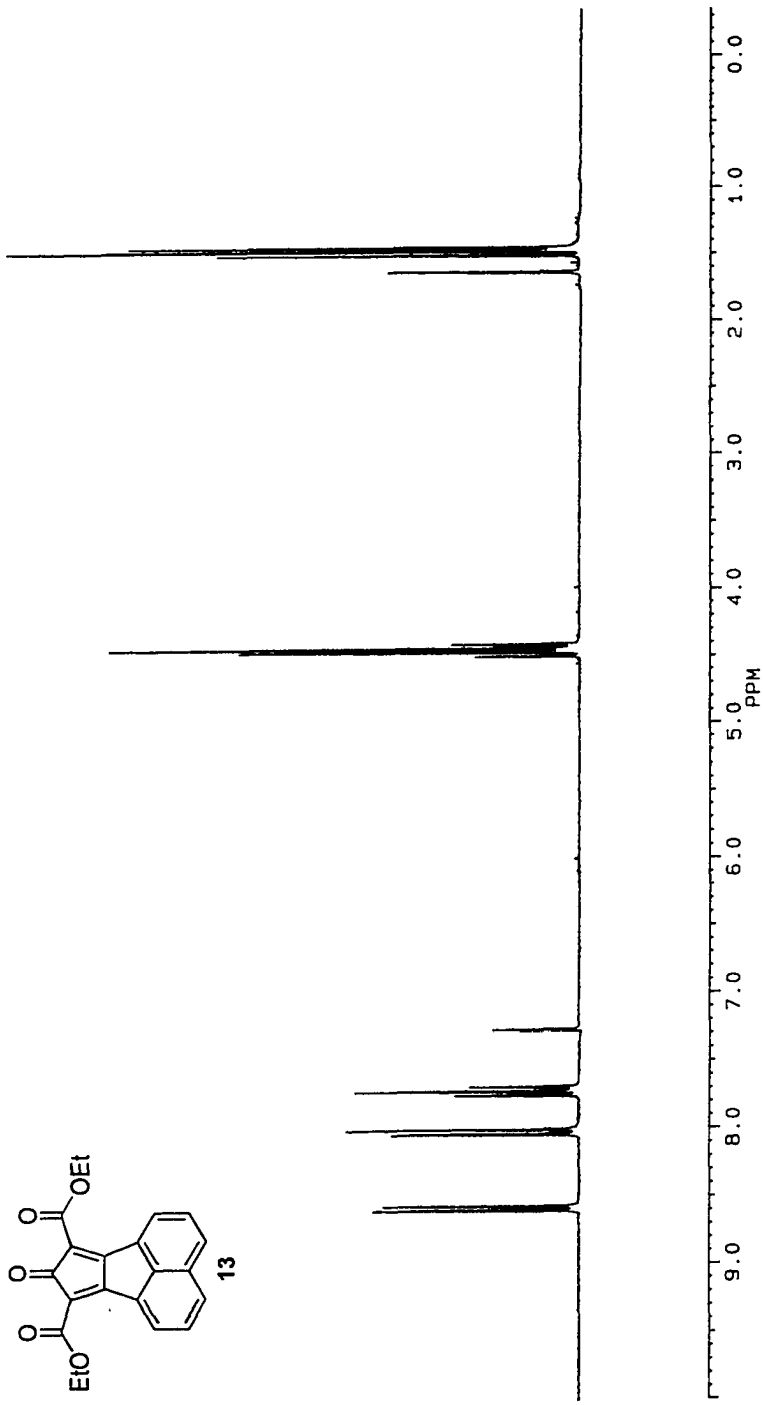
Appendix 4 250 MHz ^{1}H NMR Spectrum of 7,8a-diacetyl-9,14-dihydro-9-14-ethenocycloocta-[1,5]cyclopent[1,2-*a*]acenaphthylen-8(8a*H*)-one.



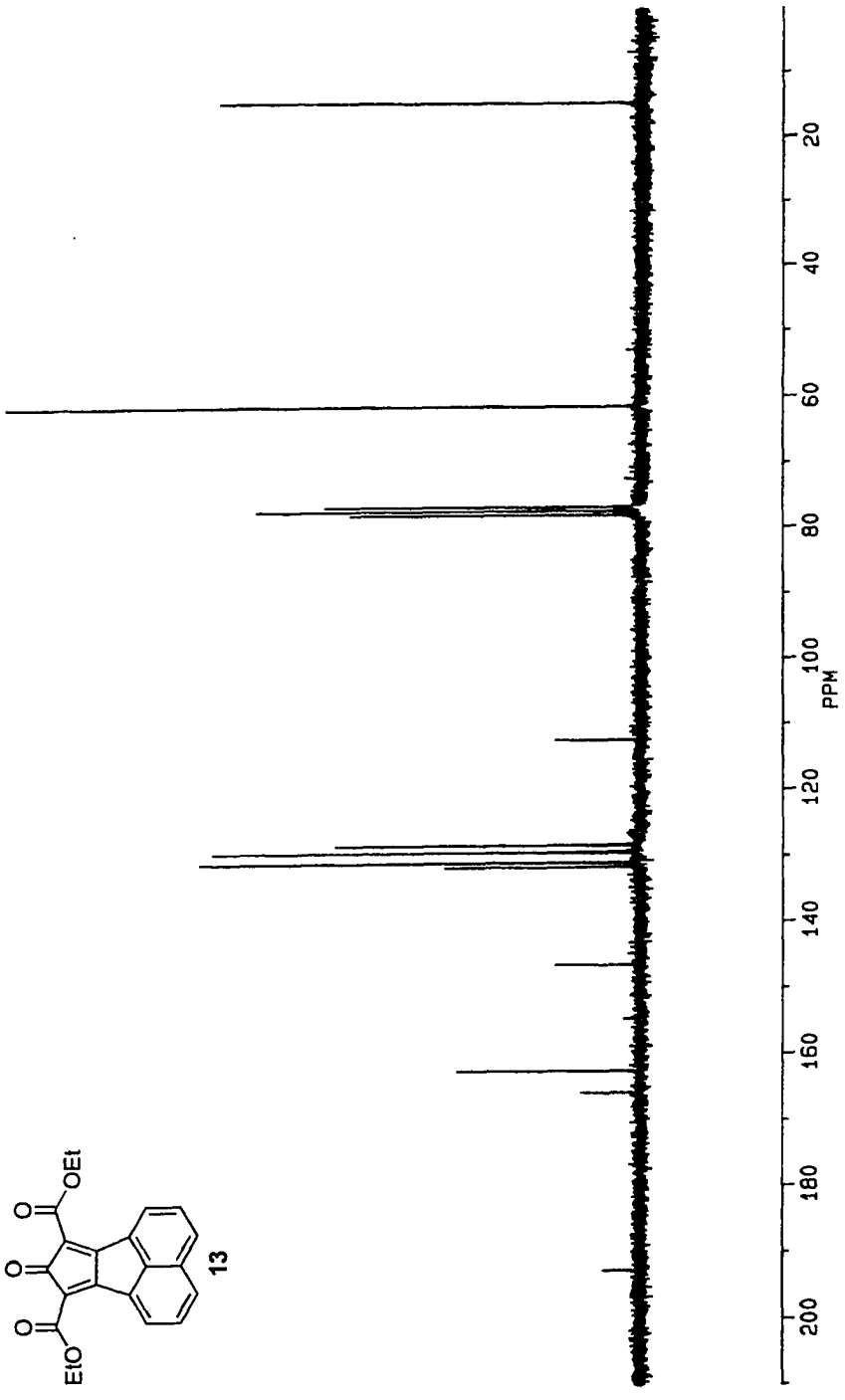
Appendix 5 62.9 MHz ^{13}C NMR Spectrum of 7,8a-diacetyl-9,14-dihydro-9-14-ethenocycloocta-[1,5]cyclopent[1,2-*a*]acenaphthylen-8(8a*H*)-one.



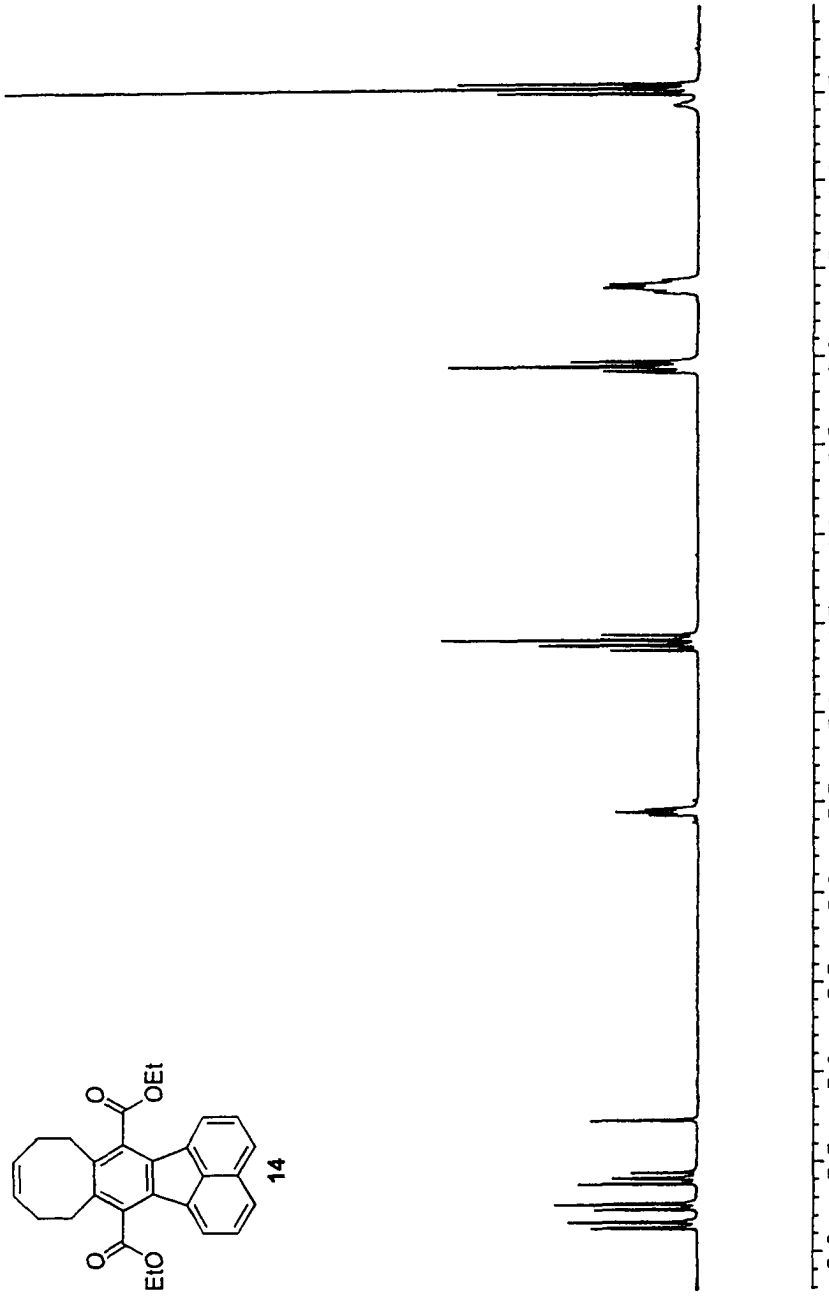
Appendix 6 Mass Spectrum of 7,8a-diacetyl-9,14-dihydro-9-14-ethenocycloocta-[1,5]cyclopent[1,2-*a*]acenaphthylen-8(8a*H*)-one.



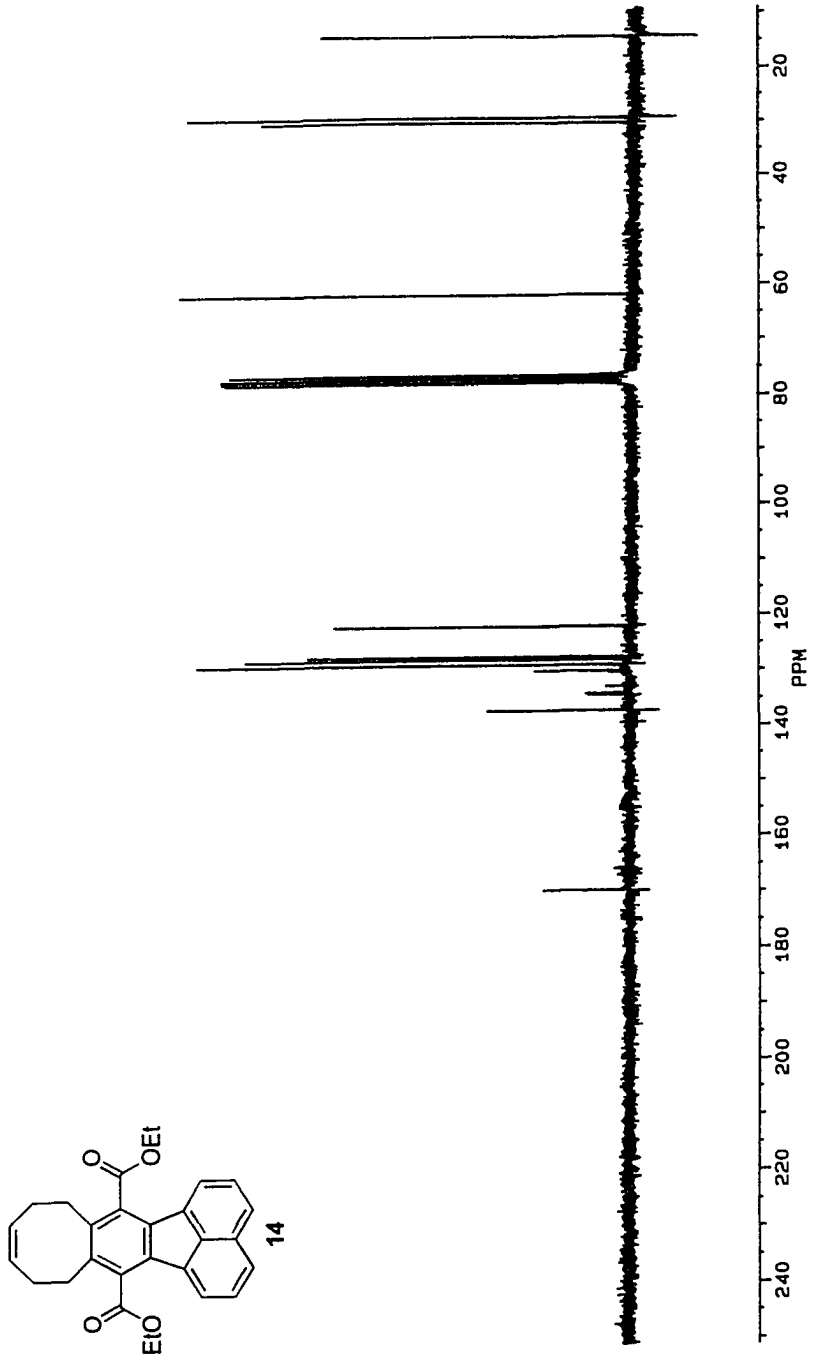
Appendix 7 250 MHz ^{1}H NMR of 5,7-diacetyl-cyclopent[*a,fg*]-acenapthylene-6-one.



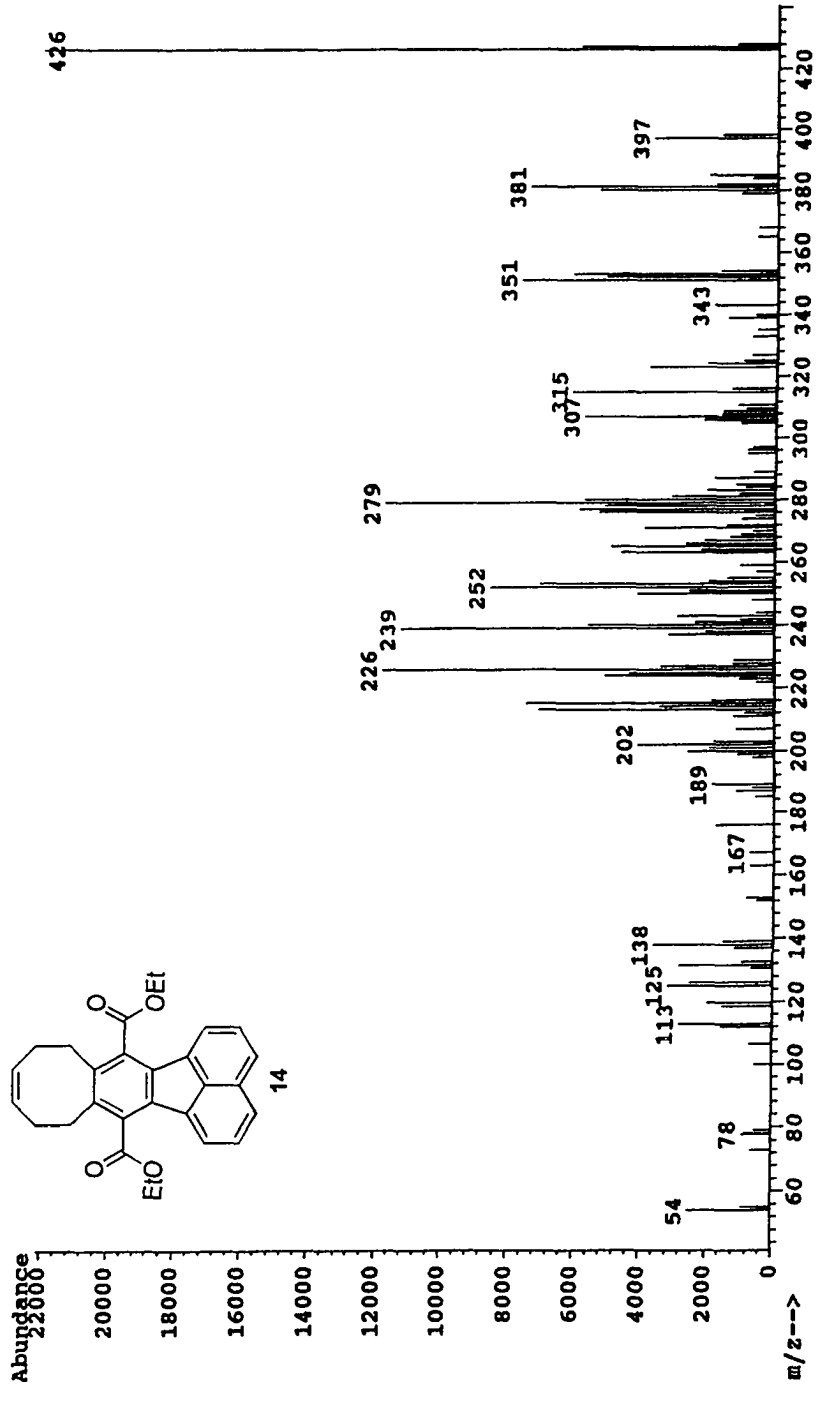
Appendix 8 50.3 MHz ^{13}C NMR of 5,7-diacetyl-cyclopent[*a,fg*]-acenapthylene-6-one.



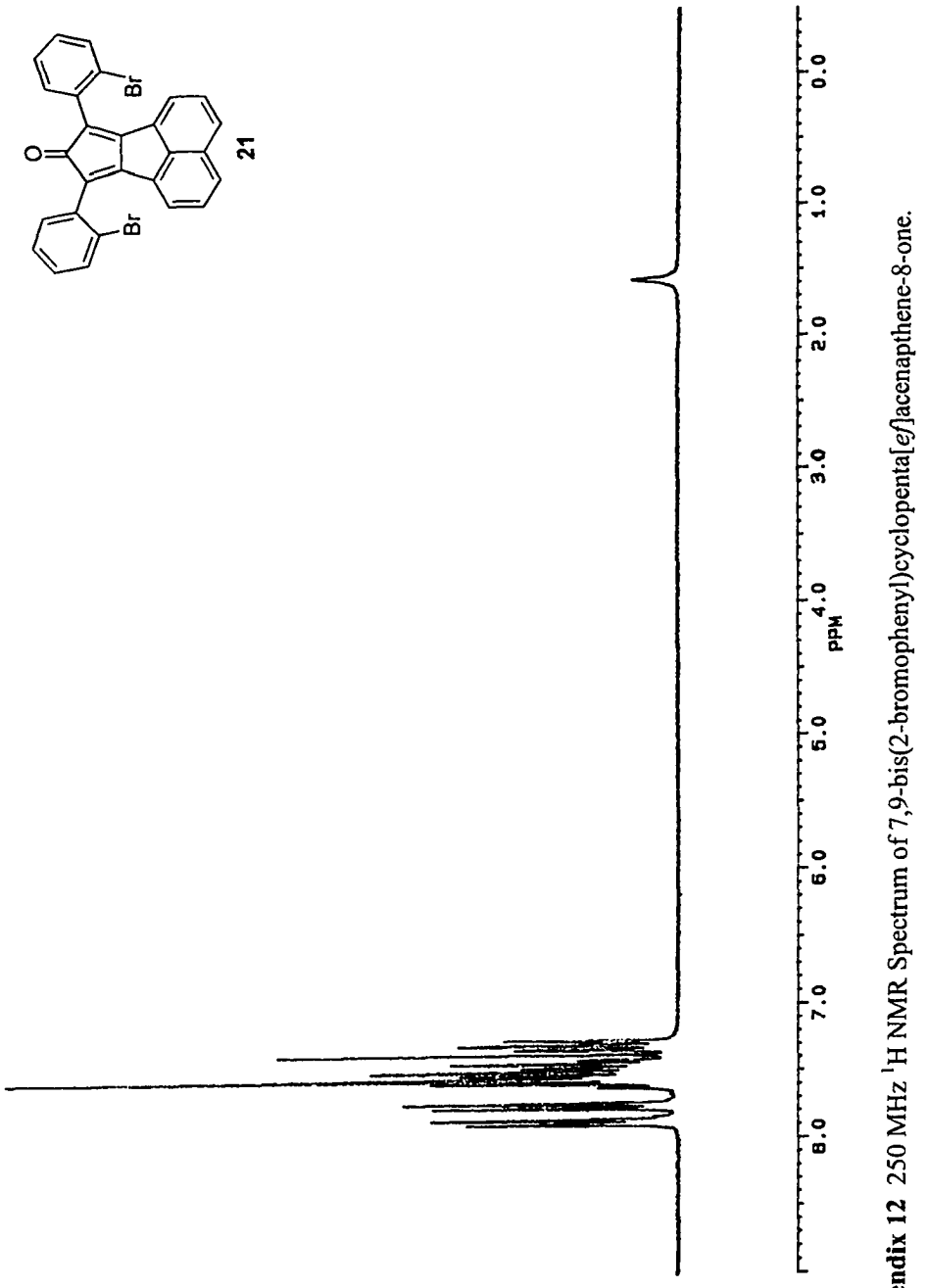
Appendix 9 250 MHz ^{1}H NMR Spectrum of **14**.



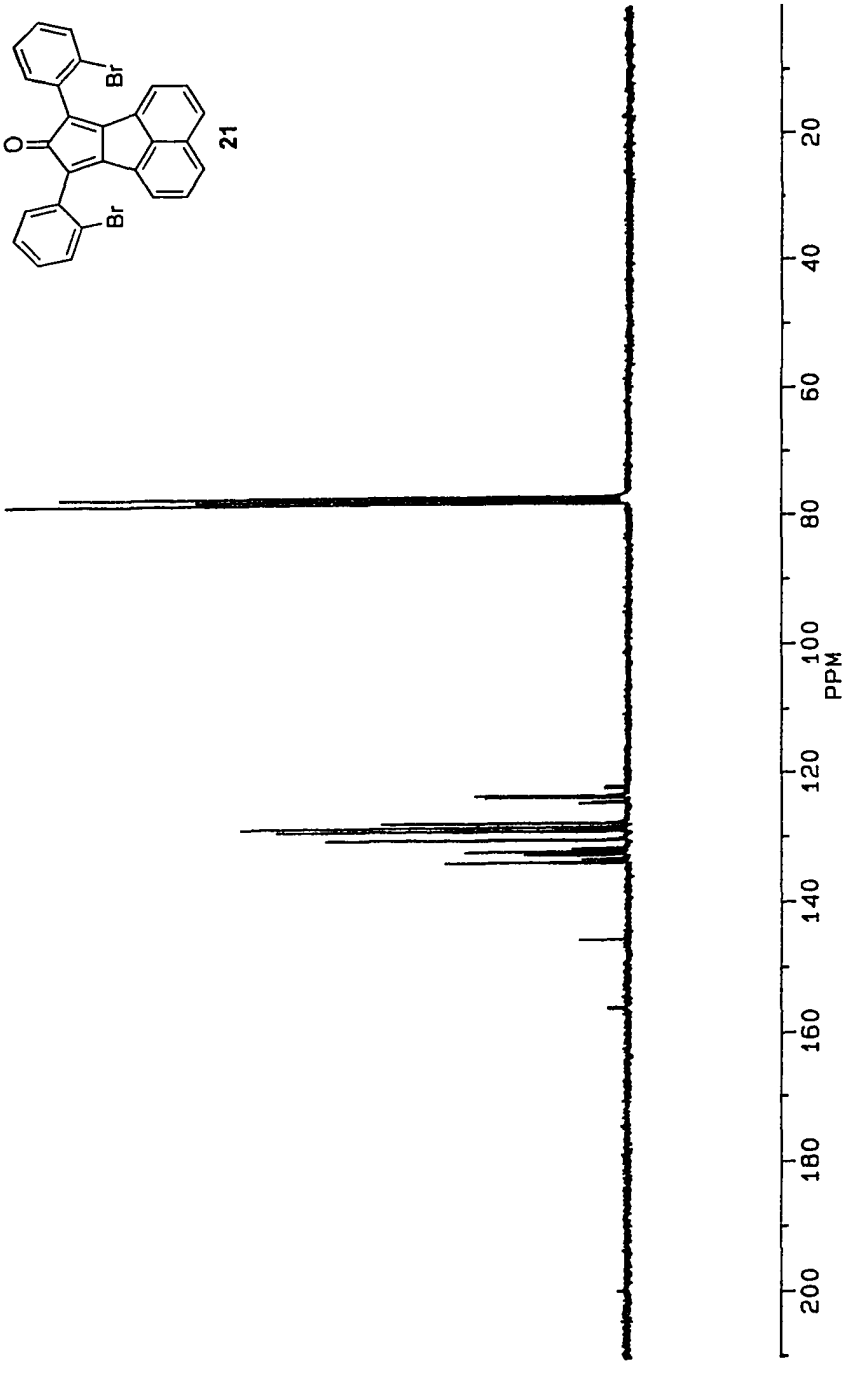
Appendix 10 62.9 MHz ^{13}C NMR Spectrum of **14**.



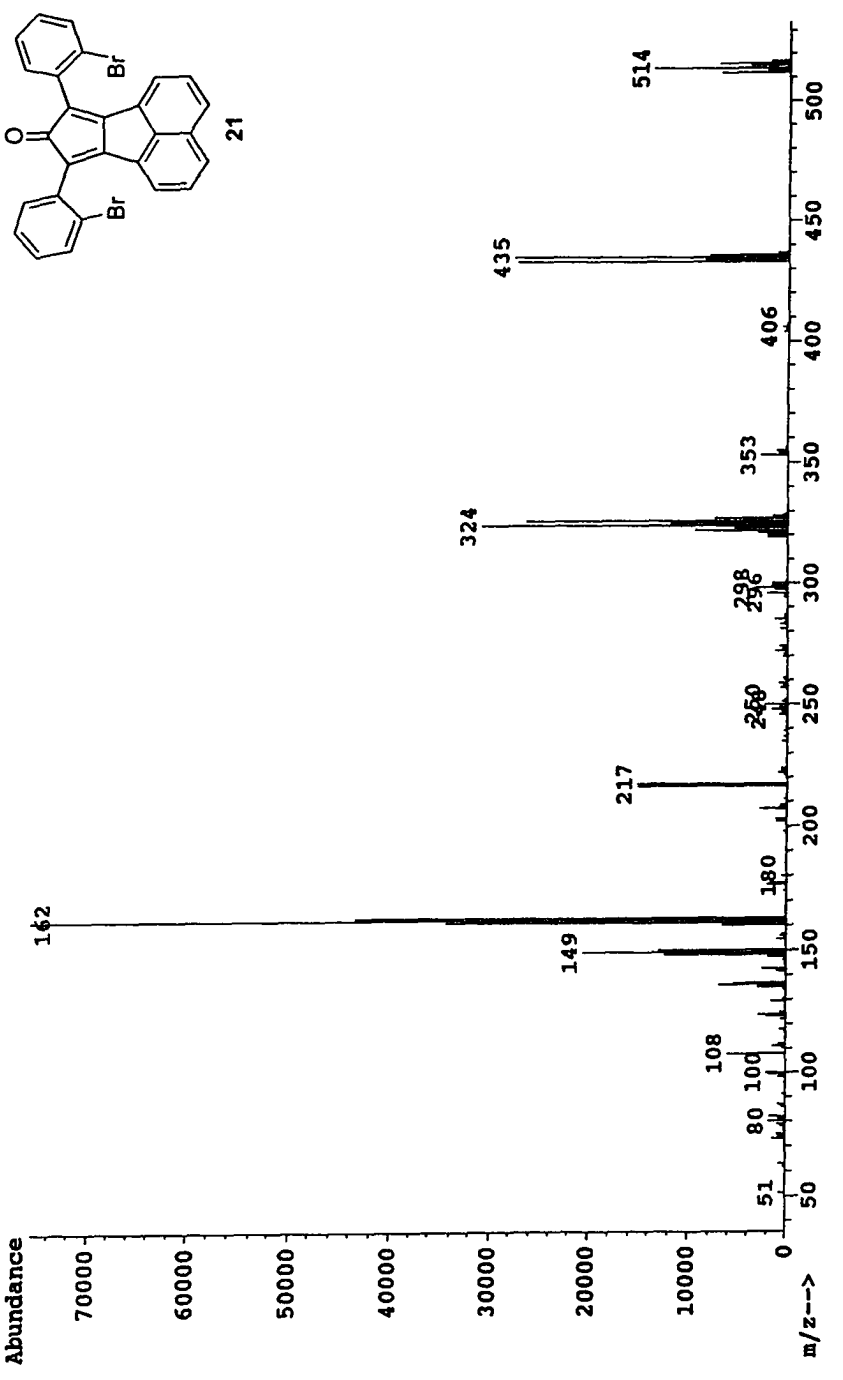
Appendix 11 Mass Spectrum of 14.



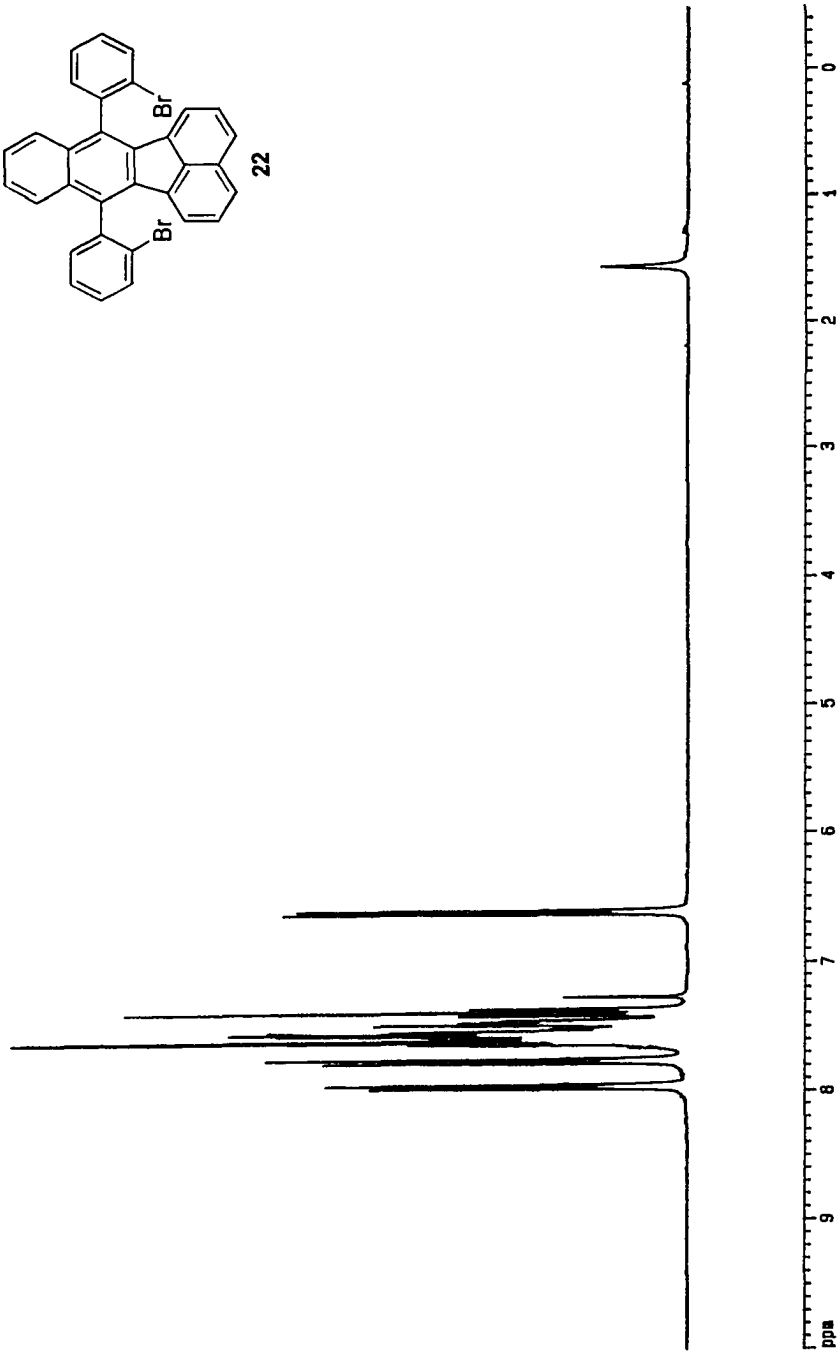
Appendix 12 250 MHz ^{1}H NMR Spectrum of 7,9-bis(2-bromophenyl)cyclopenta[*ef*]acenapthene-8-one.



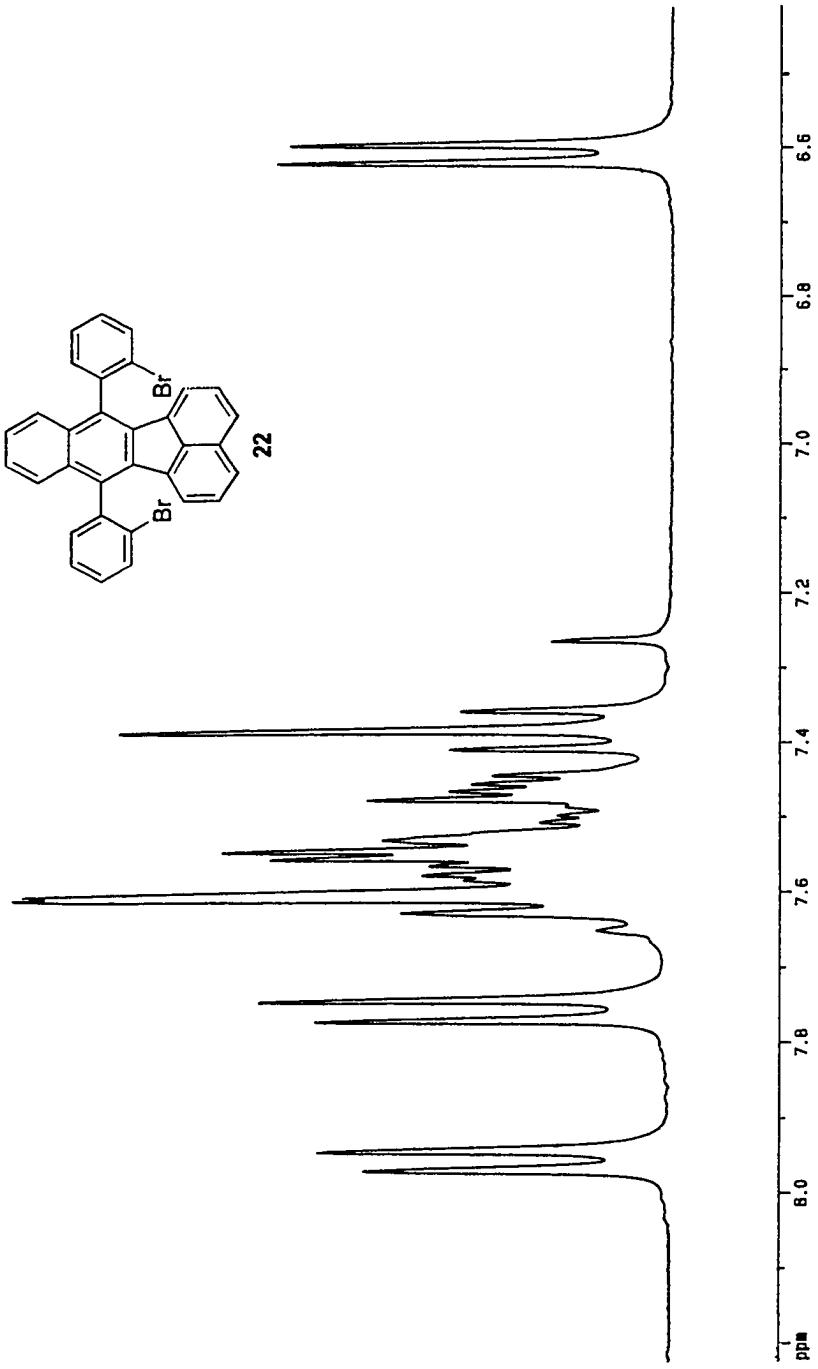
Appendix 13 75.4 MHz ^{13}C NMR Spectrum of 7,9-bis(2-bromophenyl)cyclopenta[*e*]acenapthene-8-one.



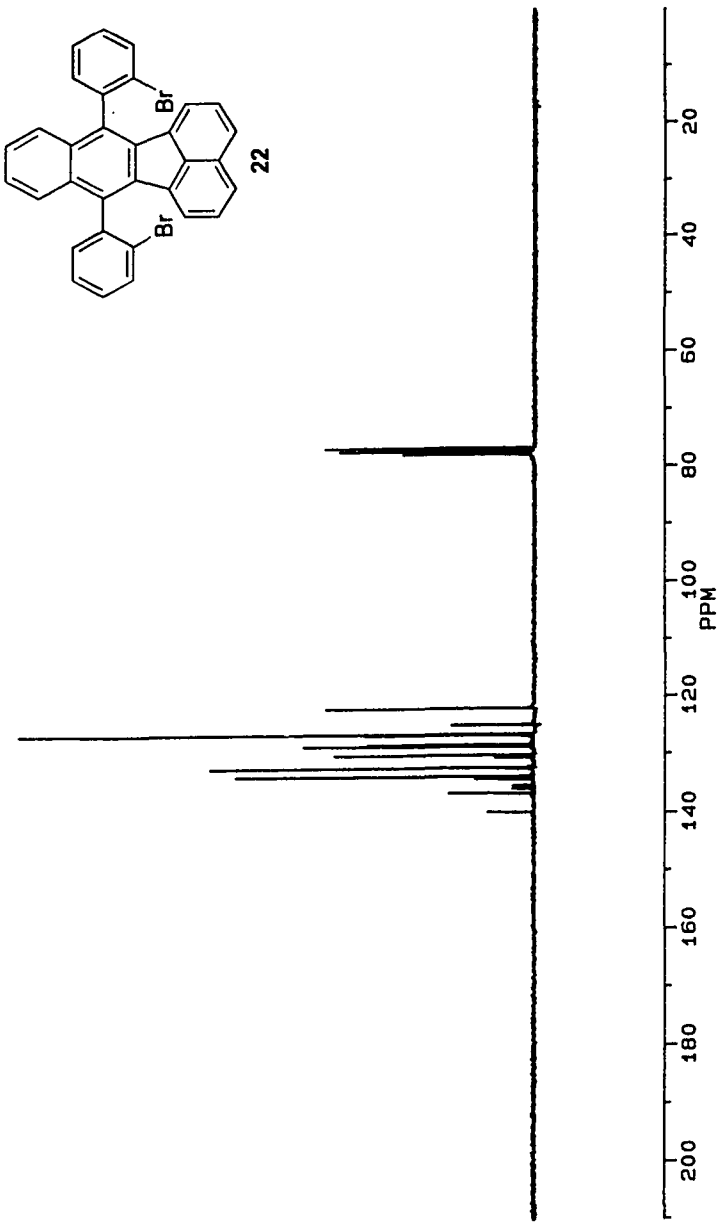
Appendix 14 Mass spectrum of 7,9-bis(2-bromophenyl)cyclopenta[*ef*]acenapthene-8-one.



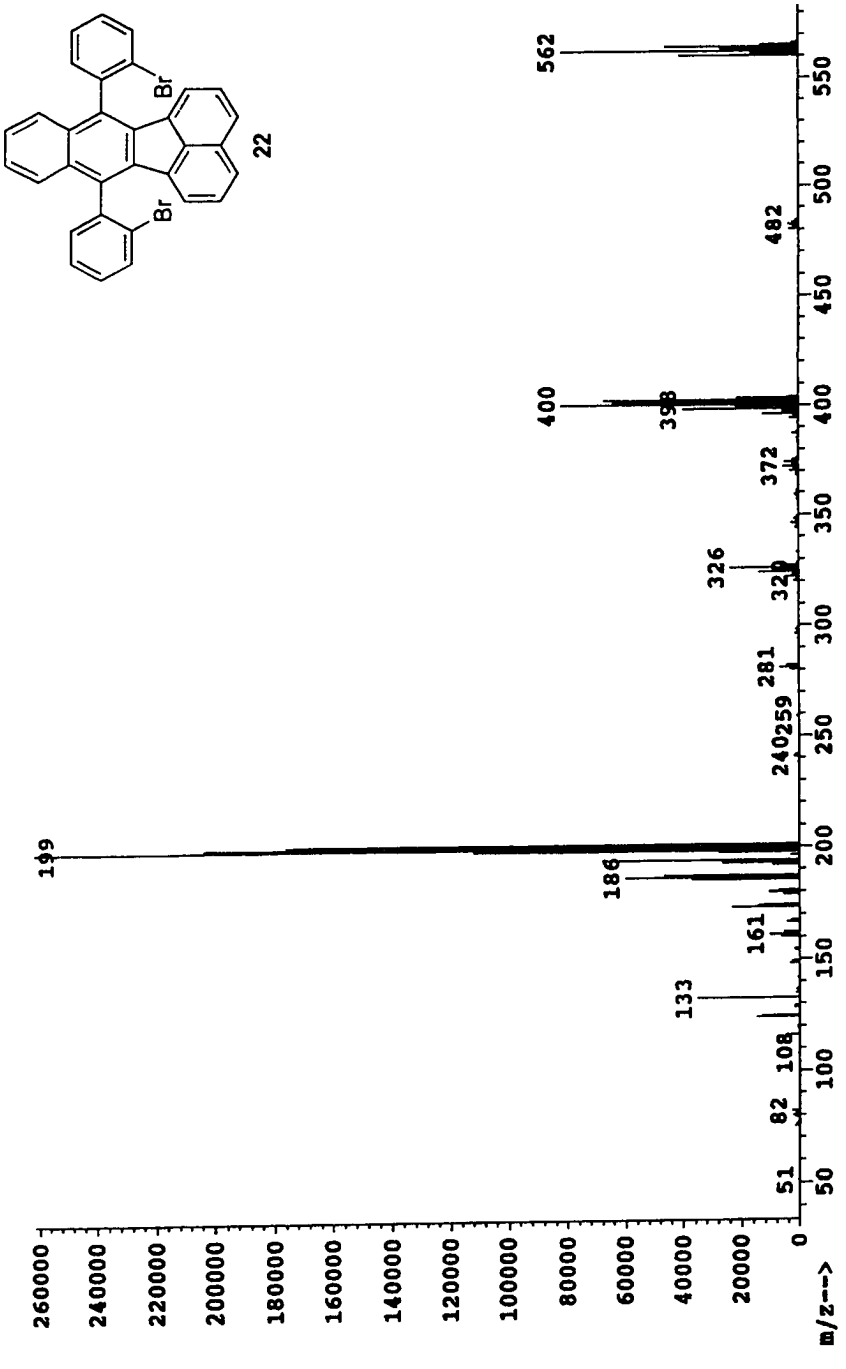
Appendix 15 300 MHz ^{1}H NMR Spectrum of 7,10-bis(2-bromophenyl)benzo[*k*]fluoranthene.



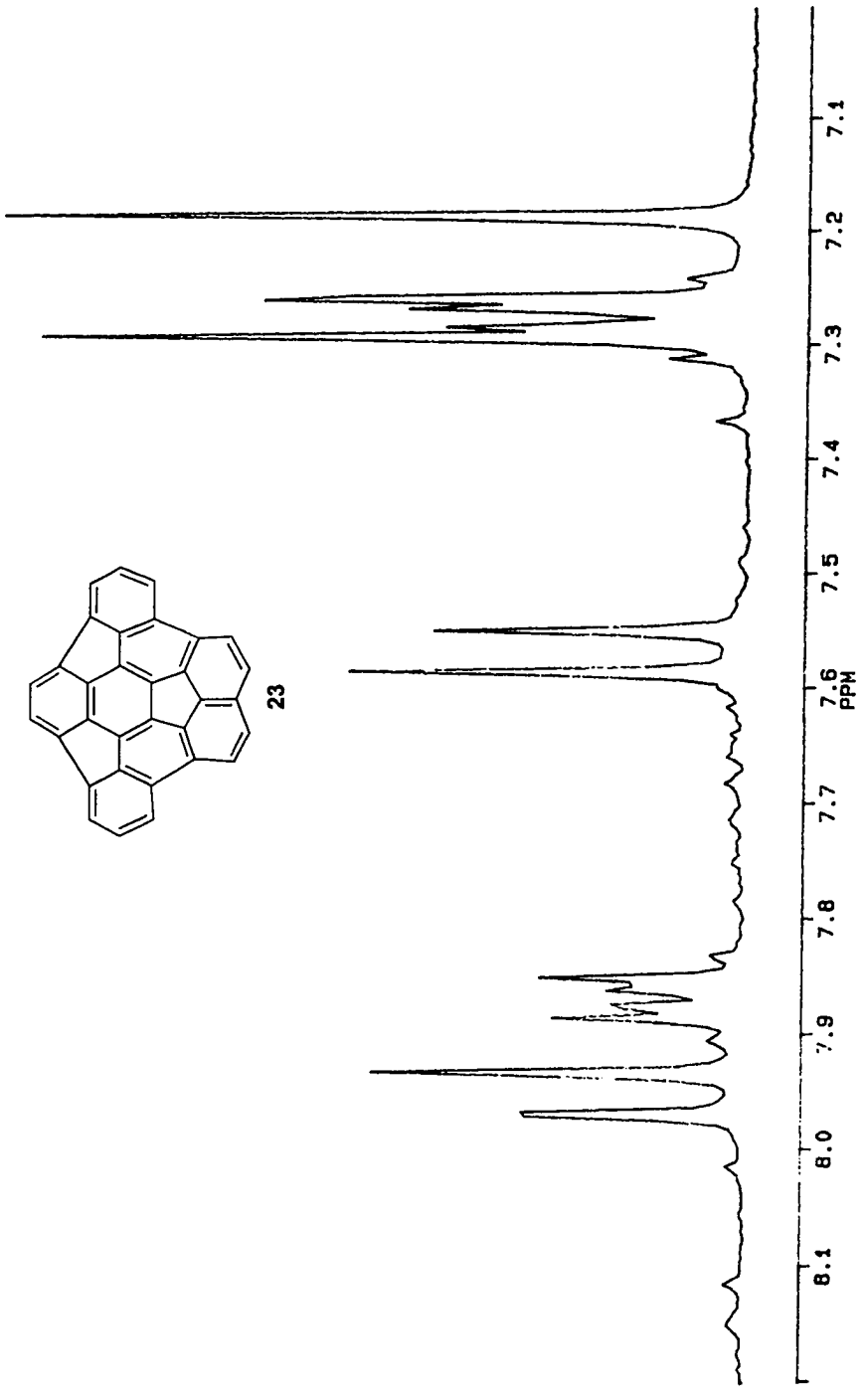
Appendix 16 Expanded 300 MHz ^{1}H MNR Spectrum of 7,10-bis(2-bromophenyl)benzo[*k*]fluoranthene.



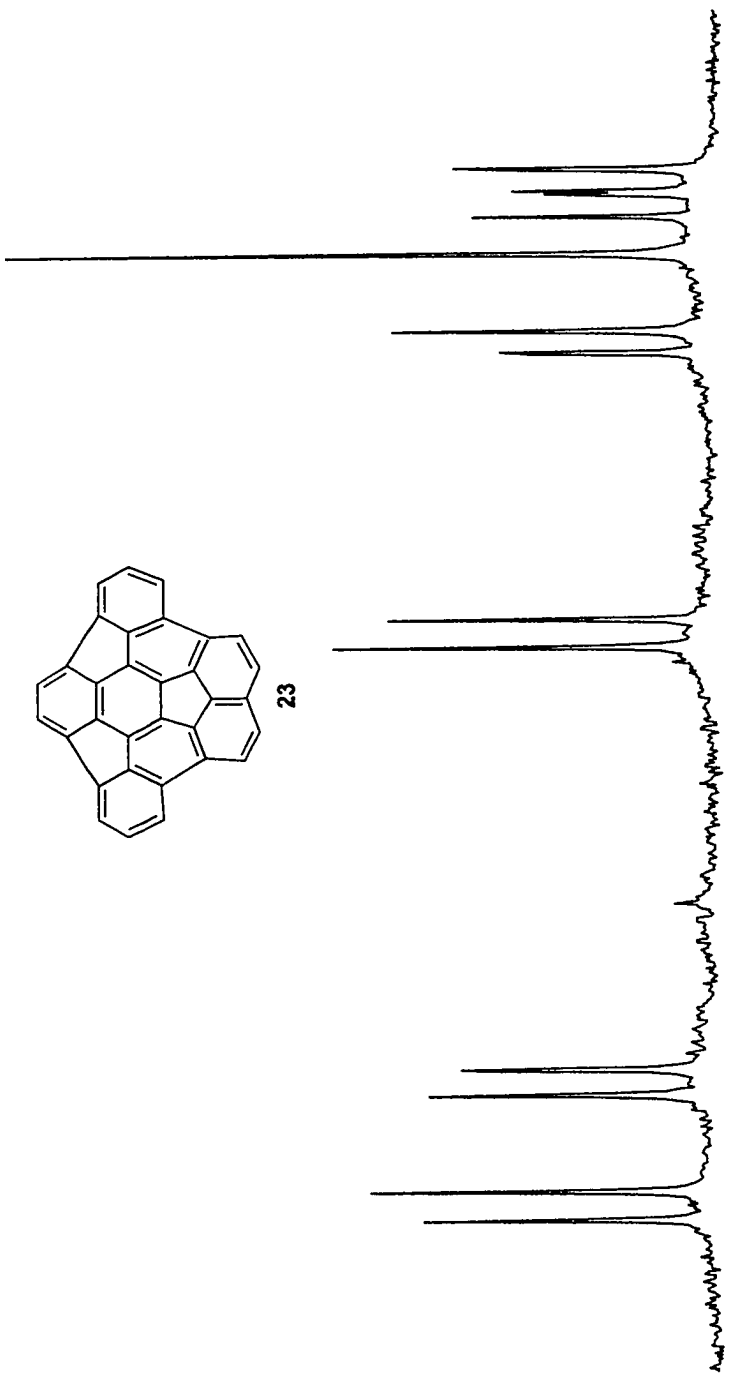
Appendix 17 62.9 MHz ^{13}C NMR Spectrum of 7,10-bis(2-bromophenyl)benzo[*k*]fluoranthene.



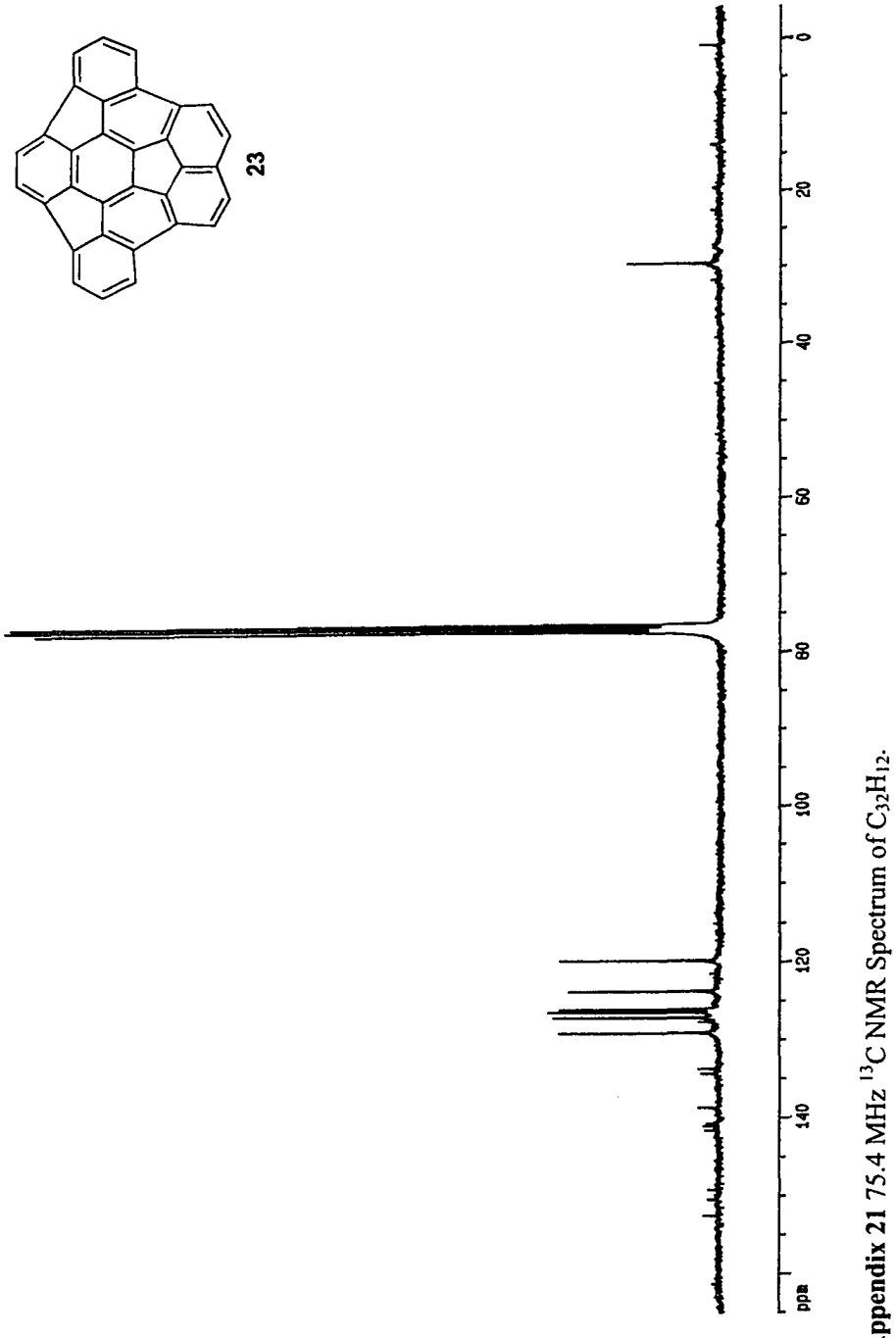
Appendix 18 Mass Spectrum of 7,10-bis(2-bromophenyl)benzo[*k*]fluoranthene.



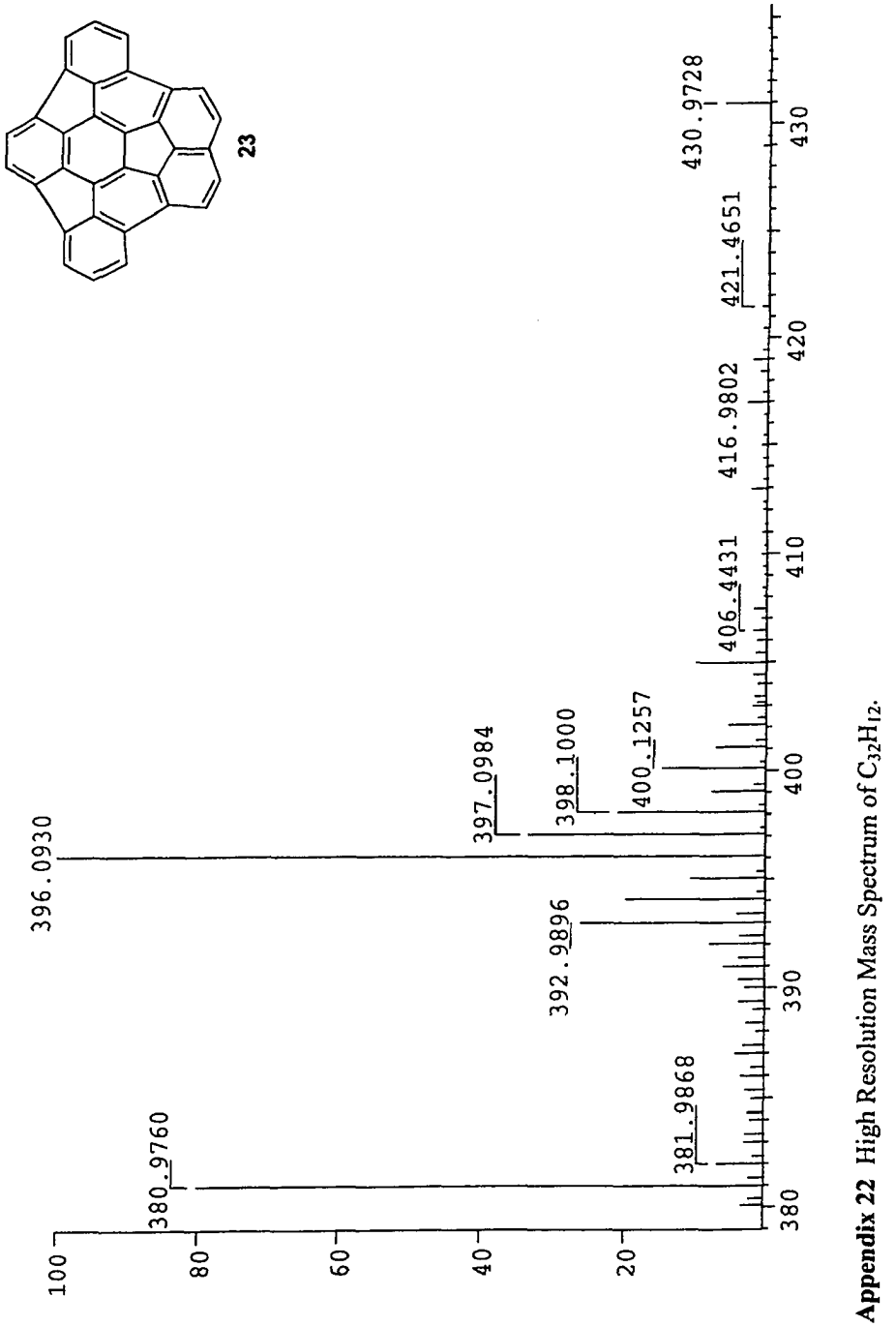
Appendix 19 250 MHz ^{1}H NMR Spectrum of $C_{32}H_{12}$ done in $CDCl_3$



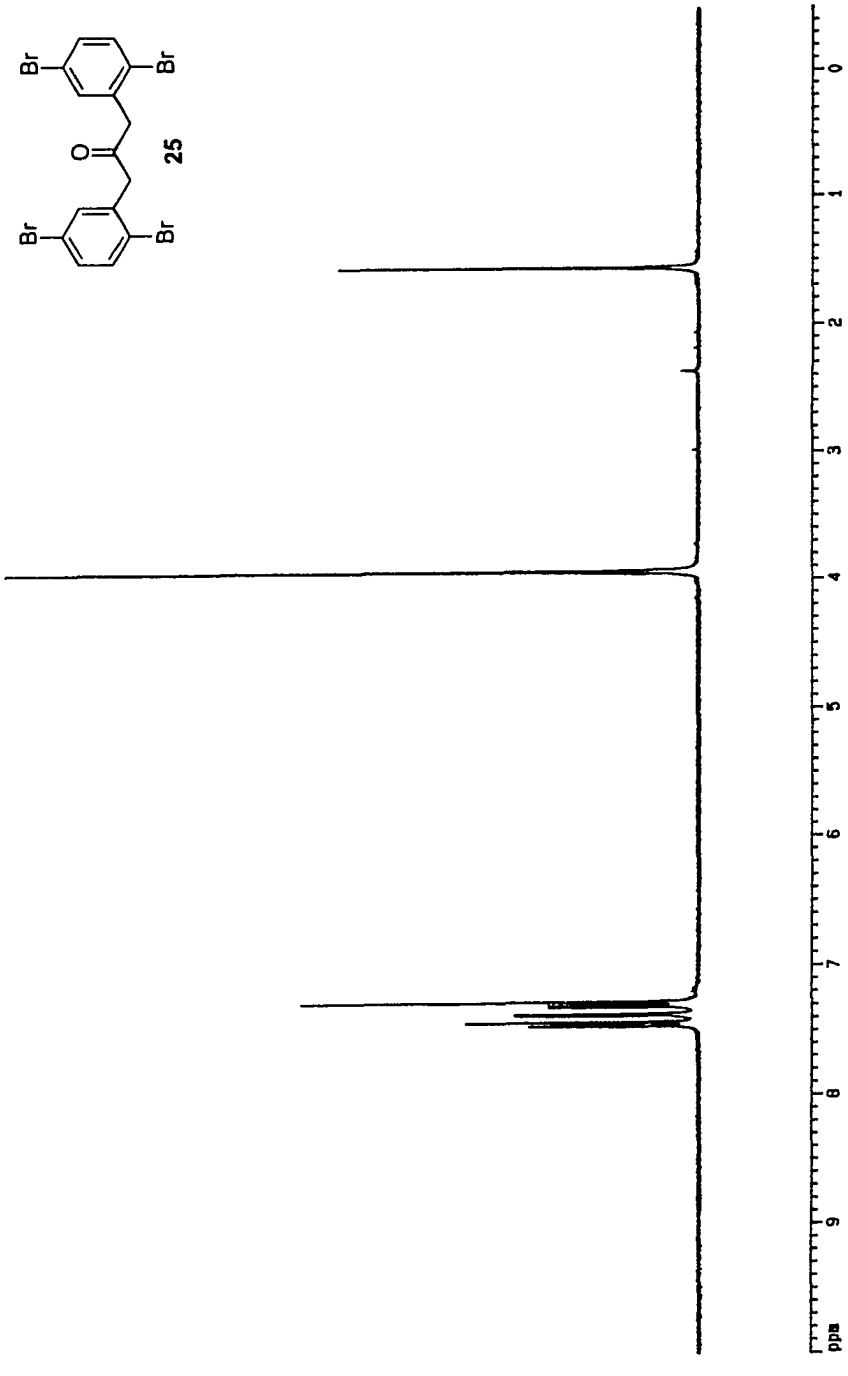
Appendix 20 400 MHz ^{1}H NMR Spectrum of $C_{32}H_{12}$ done in Acetone-d_6.



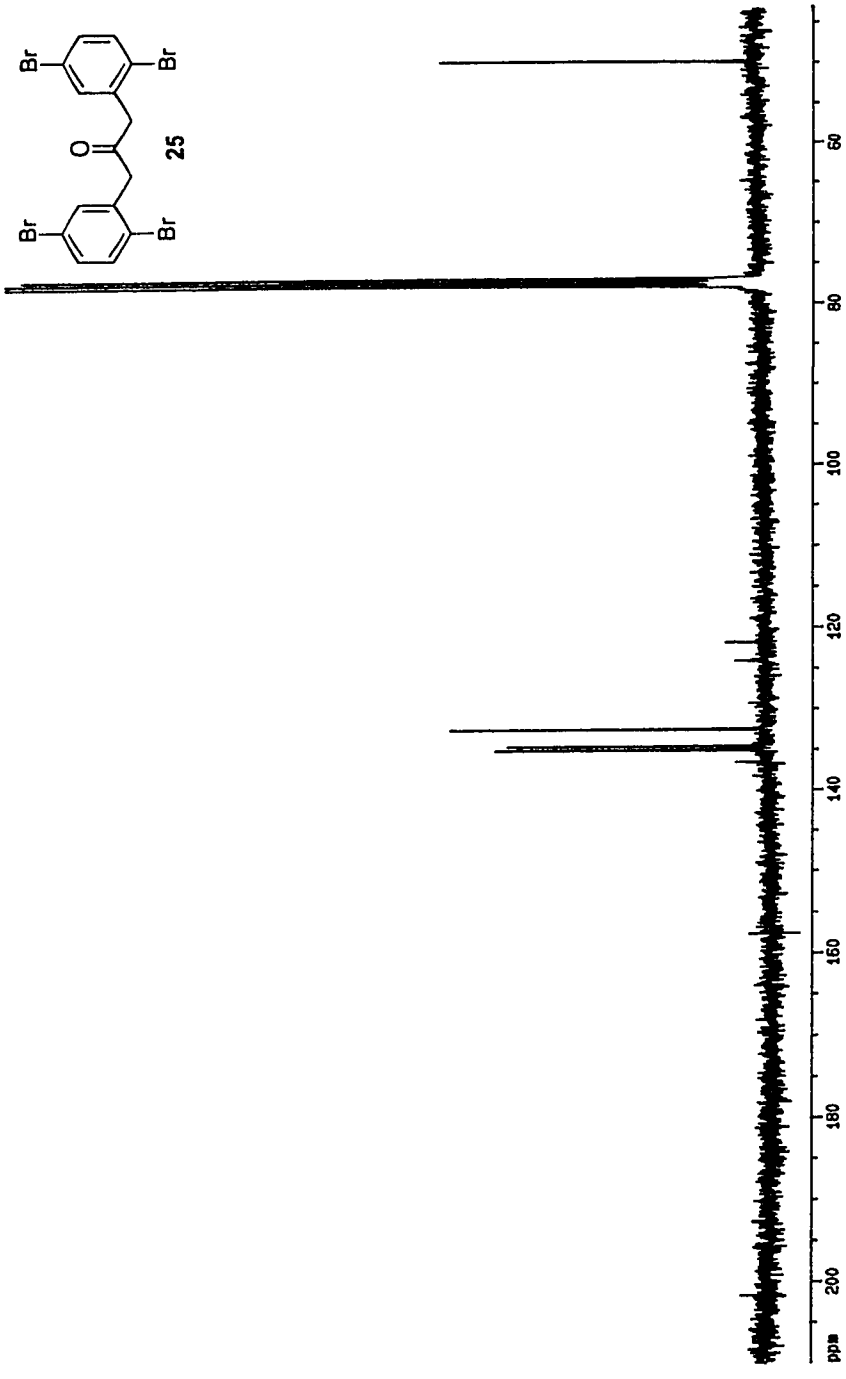
Appendix 21 75.4 MHz ^{13}C NMR Spectrum of $C_{32}H_{12}$.



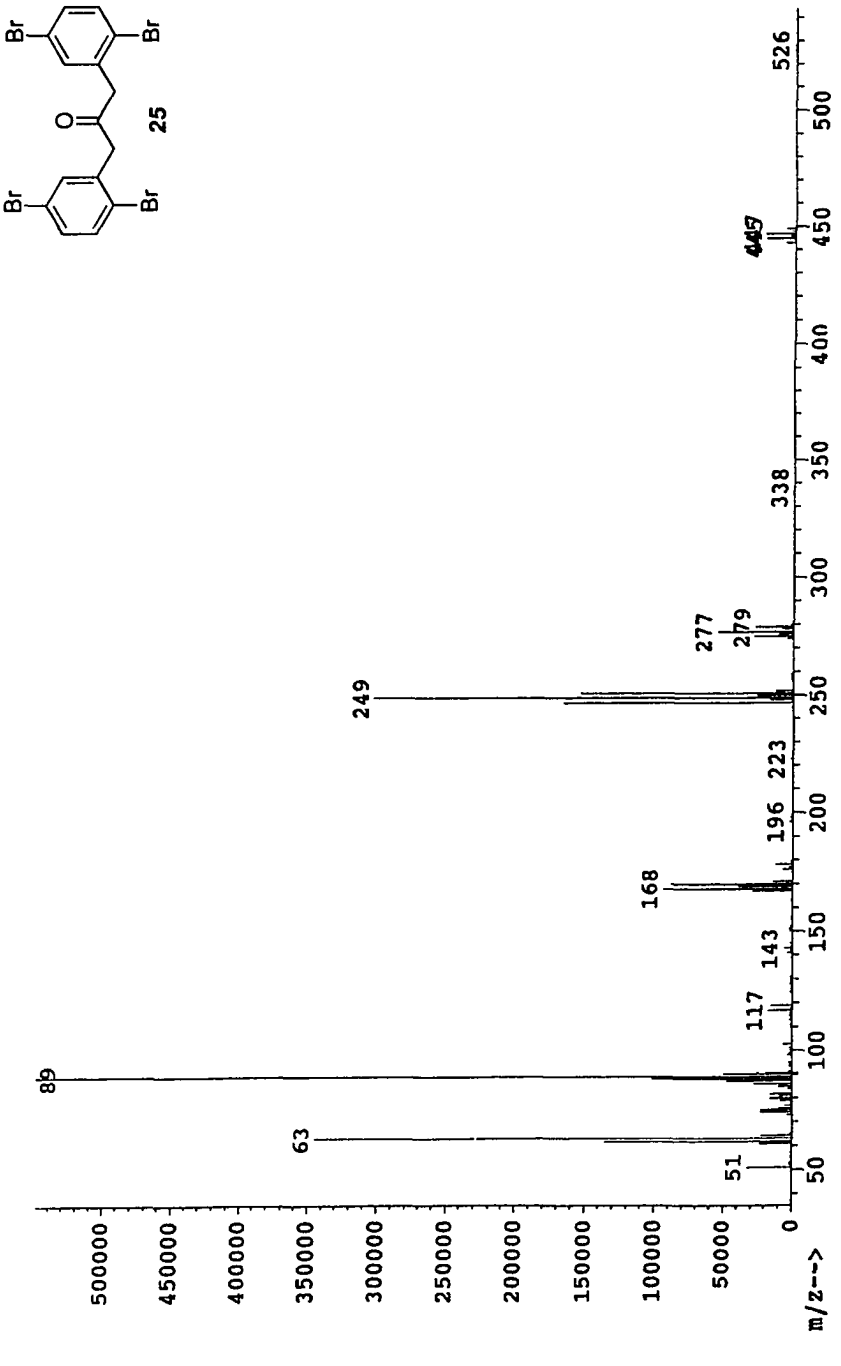
Appendix 22 High Resolution Mass Spectrum of $C_{32}H_{12}$.



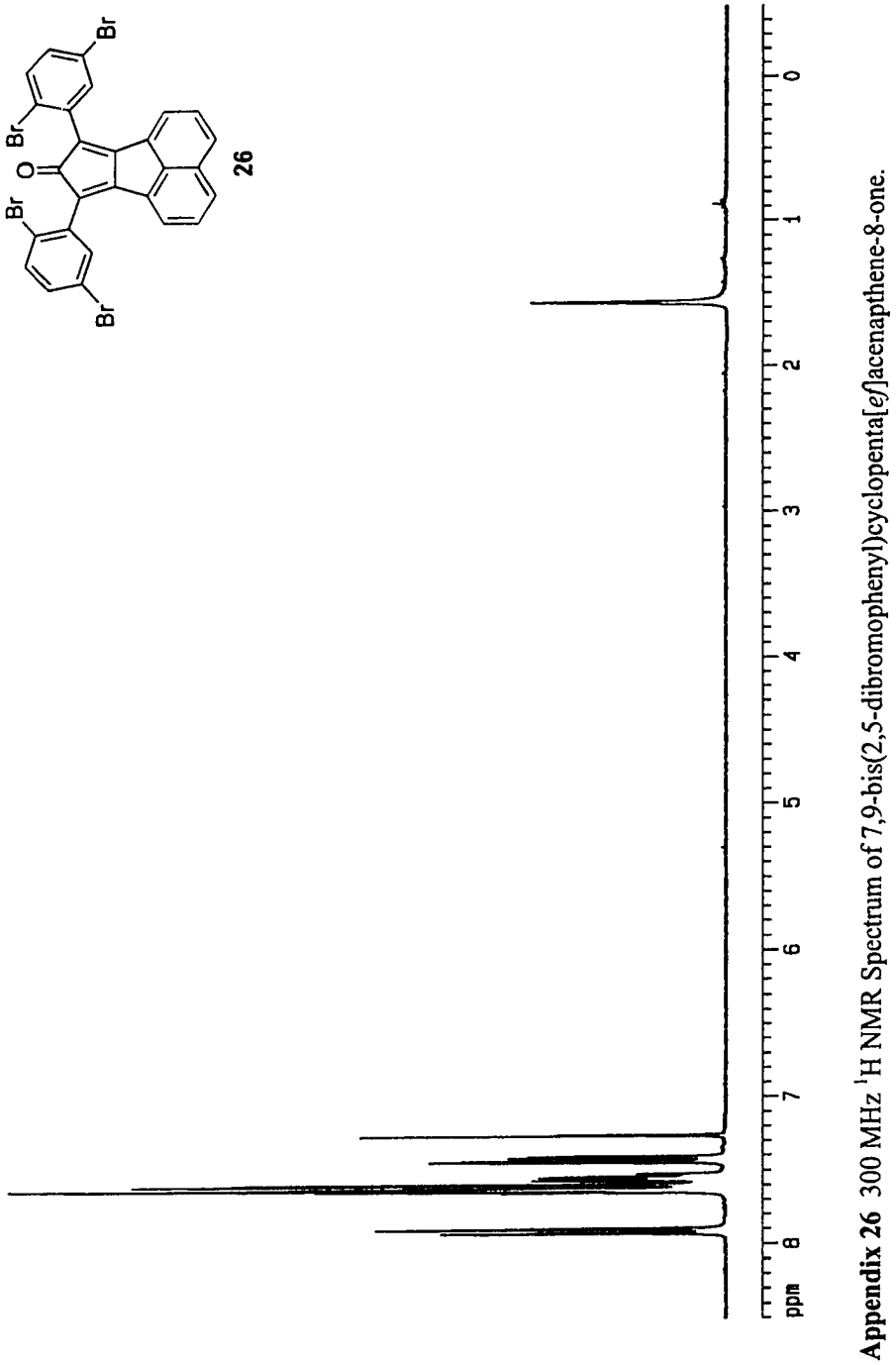
Appendix 23 300 MHz ^{1}H NMR Spectrum of 1,3-di(2,5-dibromophenyl)propan-2-one.



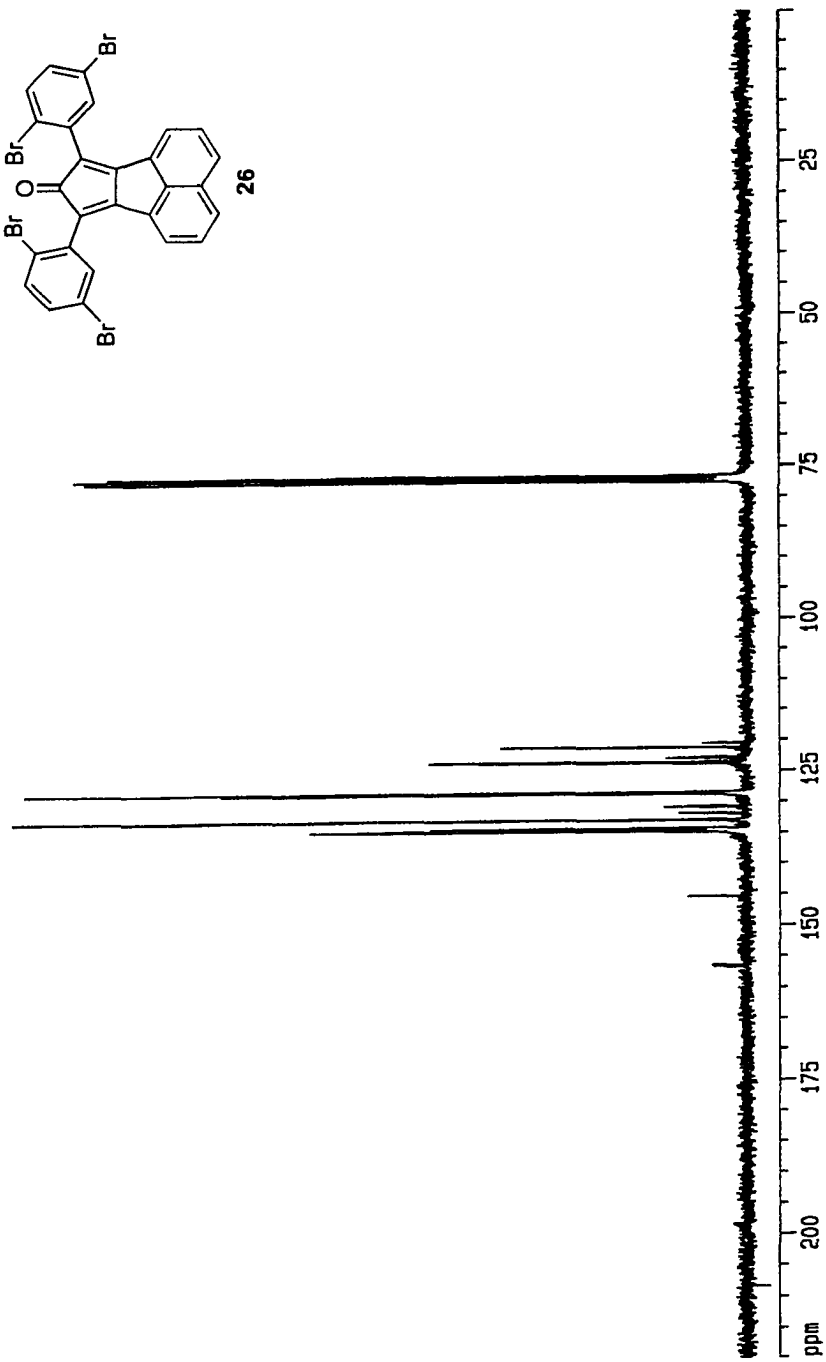
Appendix 24 62.9 MHz ^{13}C NMR Spectrum of 1,3-di(2,5-dibromophenyl)propan-2-one.



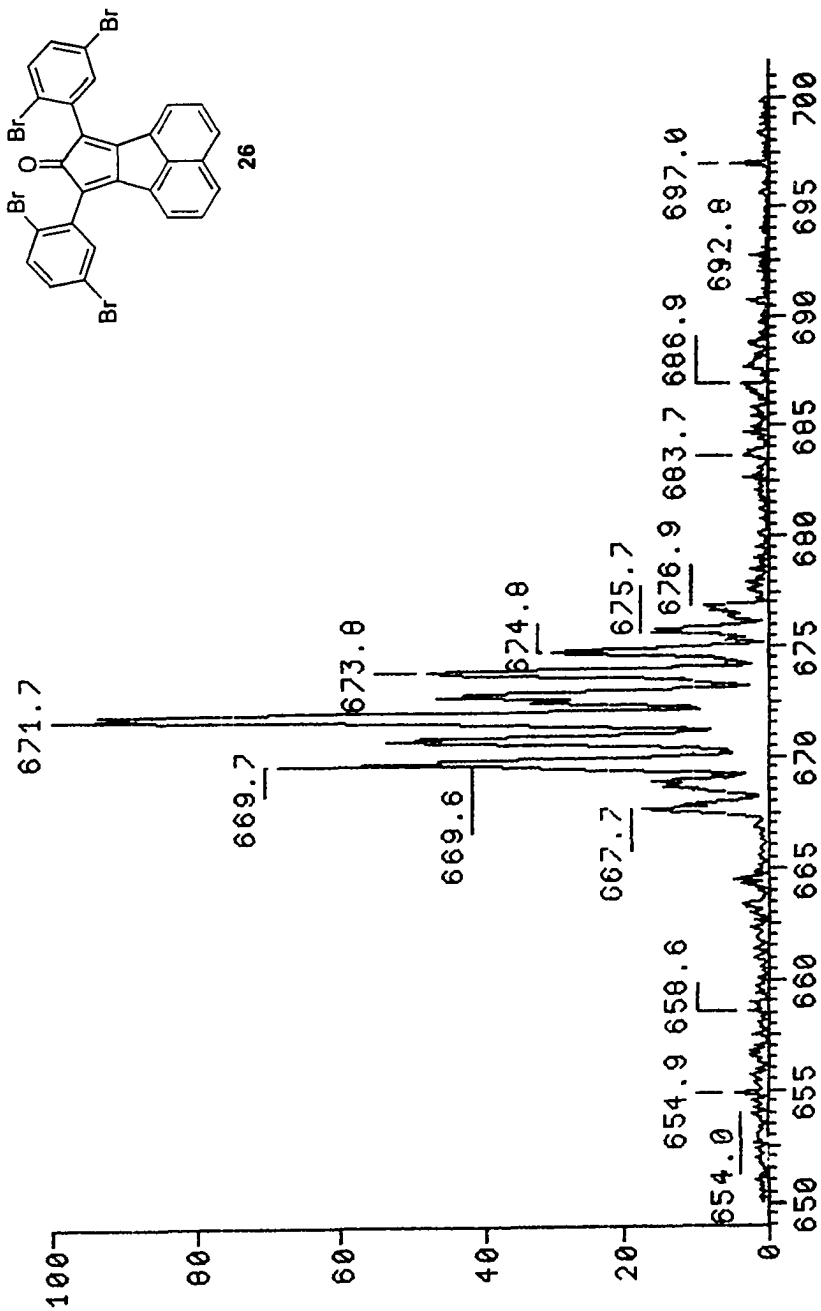
Appendix 25 Mass Spectrum of 1,3-di(2,5-dibromophenyl)propan-2-one.



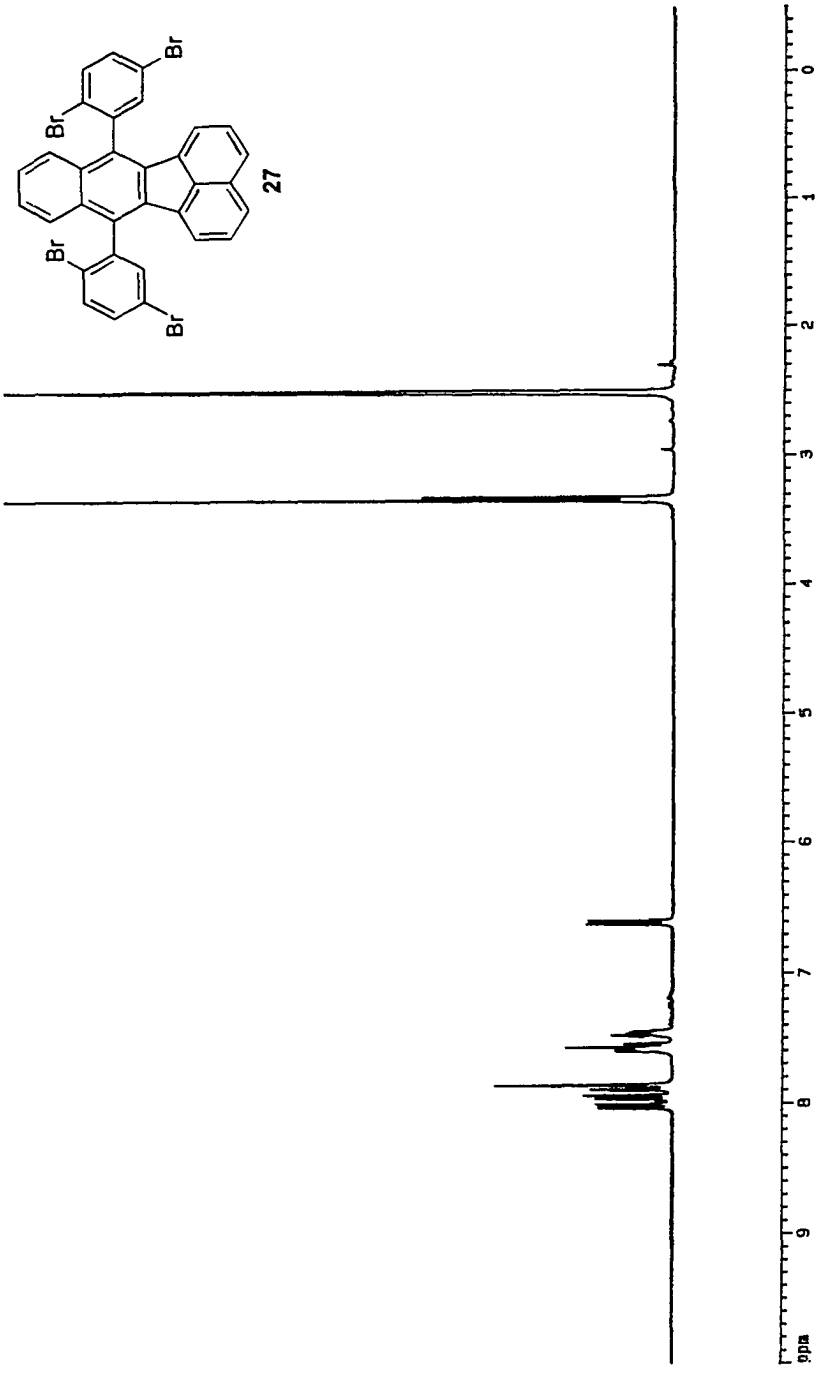
Appendix 26 300 MHz ^{1}H NMR Spectrum of 7,9-bis(2,5-dibromophenyl)cyclopenta[*ef*]acenapthene-8-one.



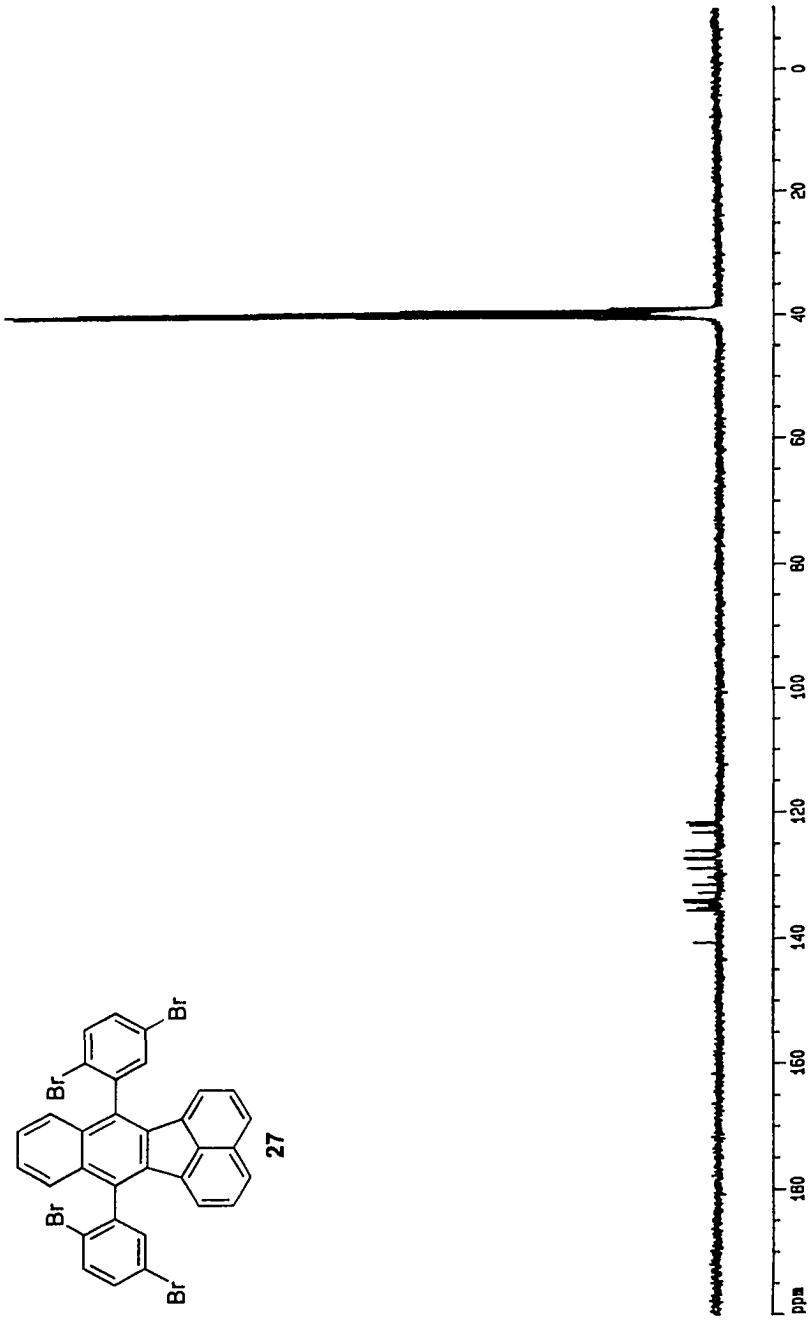
Appendix 27 75.4 MHz ^{13}C NMR Spectrum of 7,9-bis(2,5-dibromophenyl)cyclopenta[*e*]acenapthene-8-one.



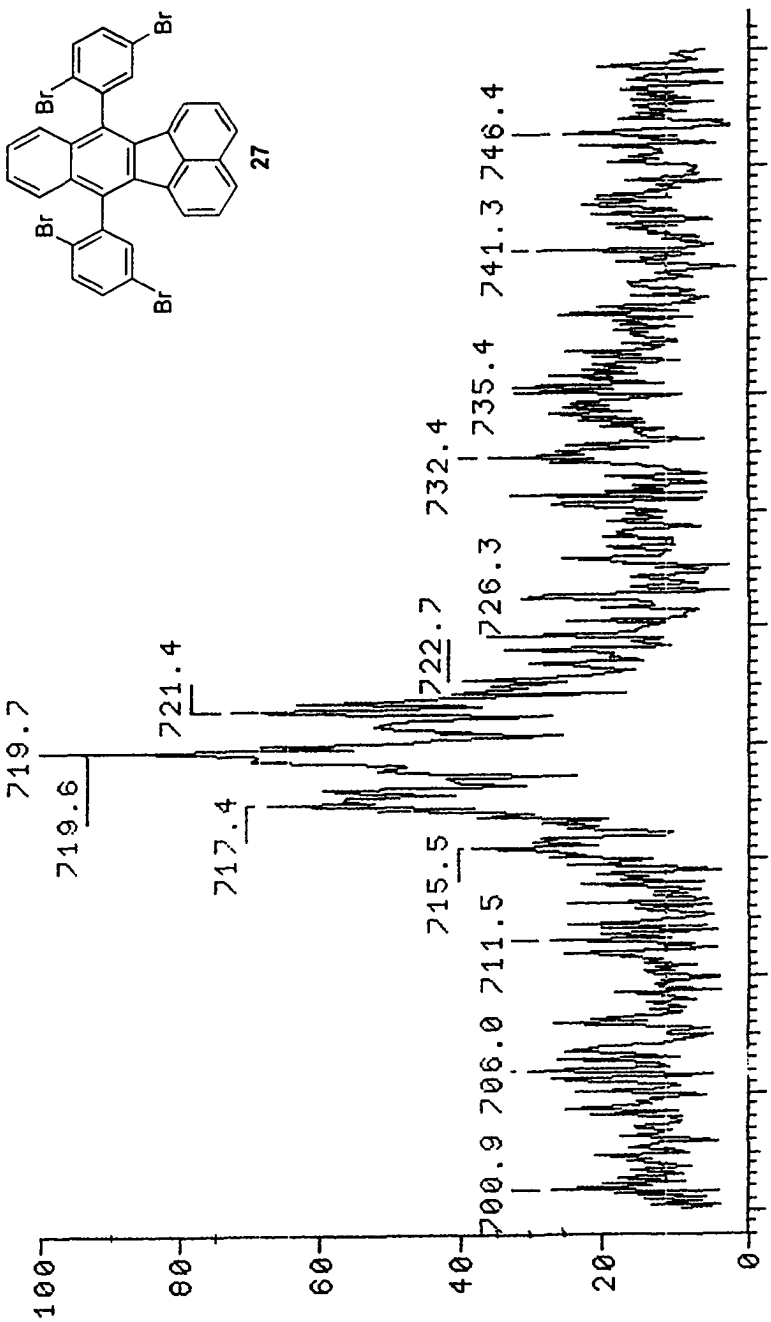
Appendix 28 FAB Mass Spectrum of 7,9-bis(2,5-dibromophenyl)cyclopenta[*ef*]acenapthene-8-one.



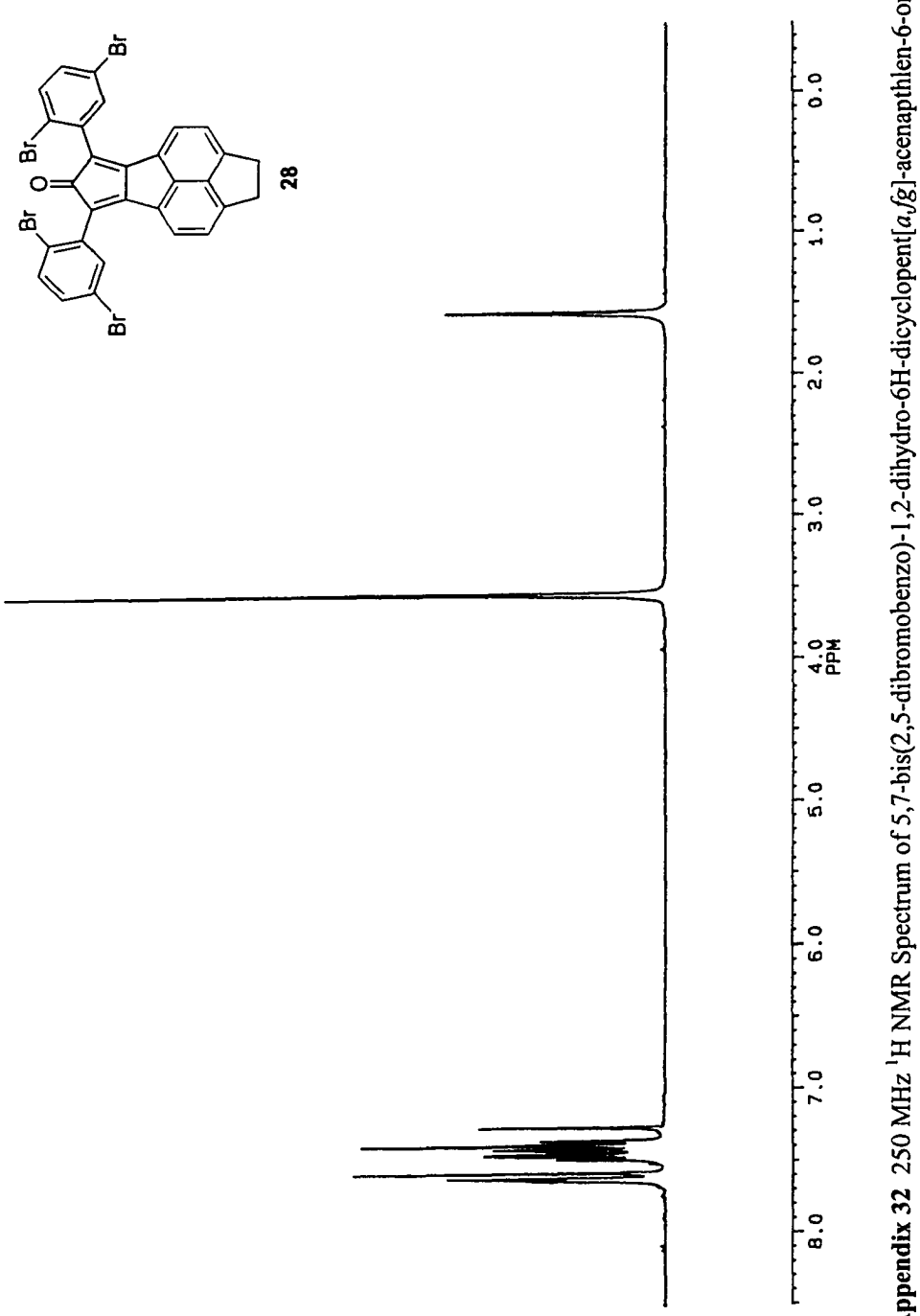
Appendix 29 300 MHz ^{1}H NMR Spectrum of 7,10-bis(2,5-dibromophenyl)benzo[*k*]fluoranthene done in DMSO-d_6.



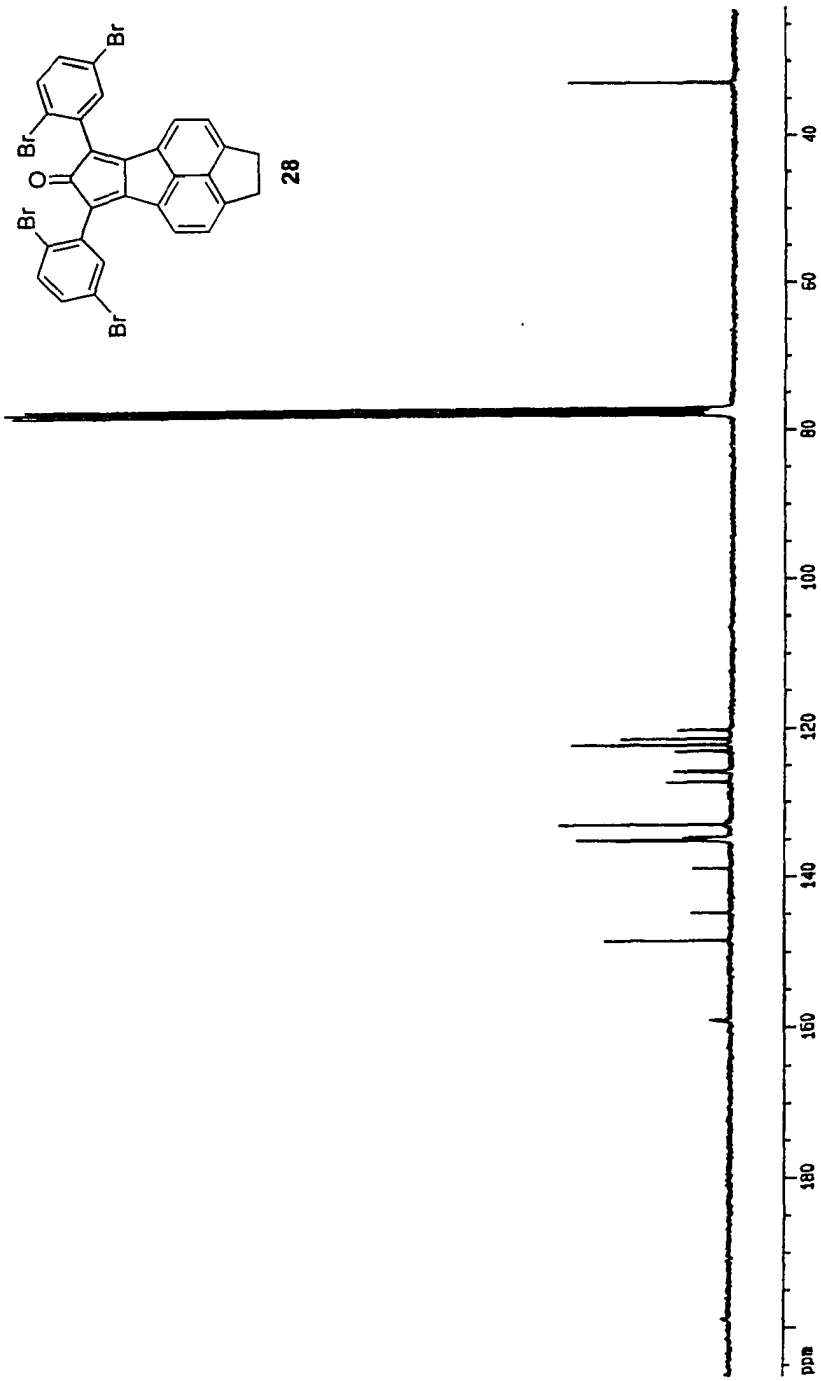
Appendix 30 75.4 MHz ^{13}C NMR Spectrum of 7,10-bis(2,5-dibromophenyl)benzo[*k*]fluoranthene done in DMSO-d_6.



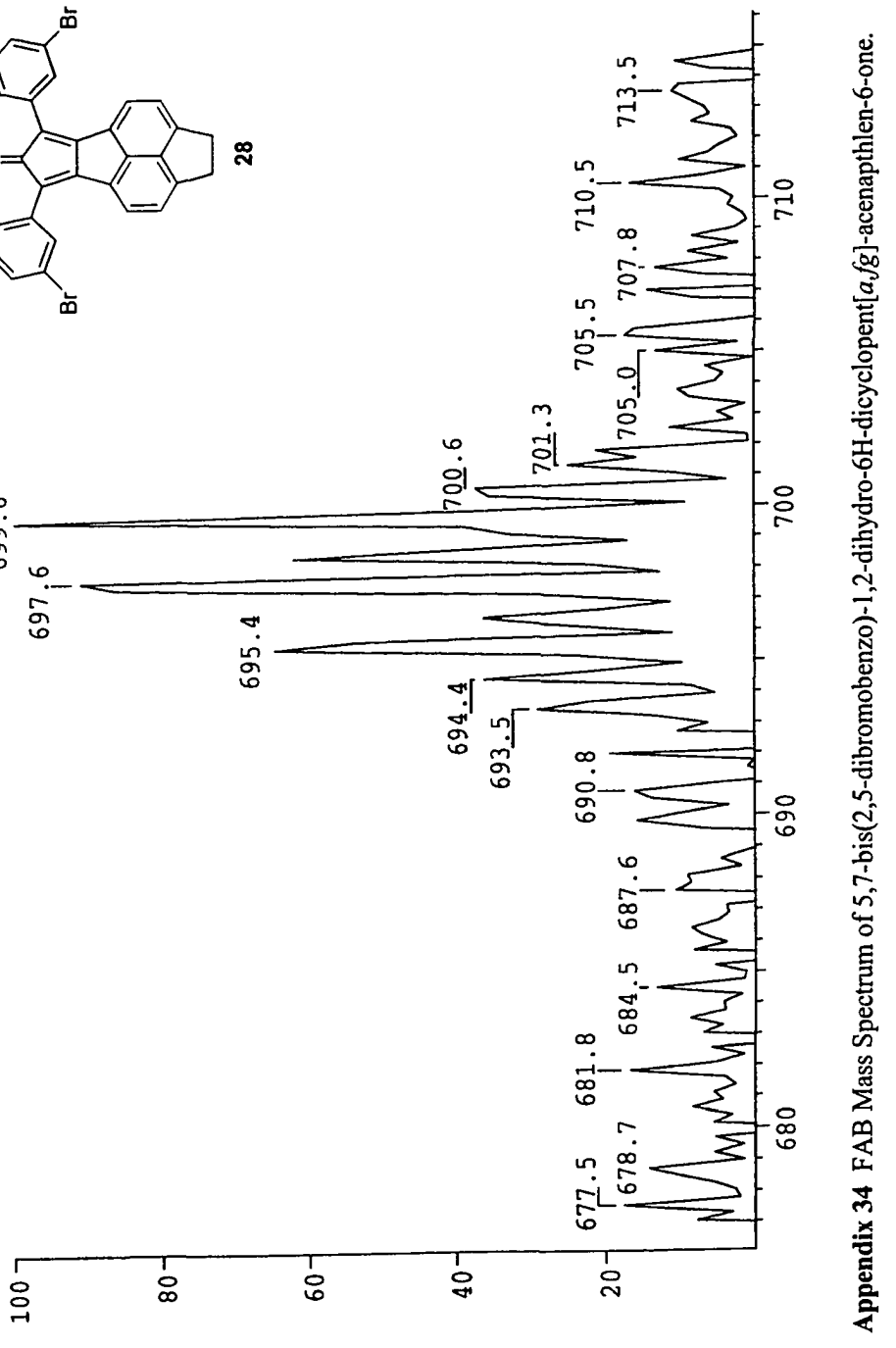
Appendix 31 FAB Mass Spectrum of 7,10-bis(2,5-dibromophenyl)benzo[*k*]fluoranthene.



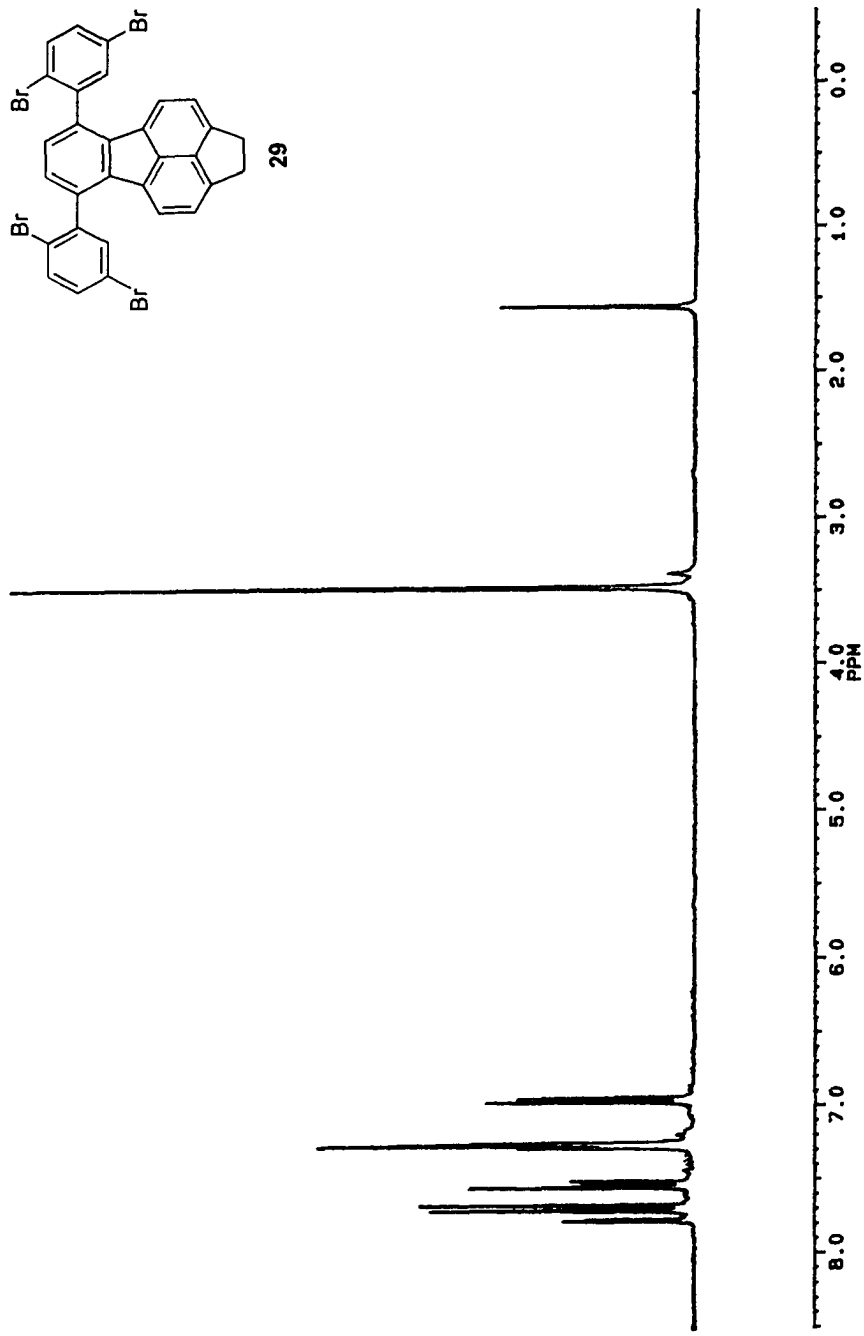
Appendix 32 250 MHz ^{1}H NMR Spectrum of 5,7-bis(2,5-dibromobenzo)-1,2-dihydro-6H-dicyclopent[*a,fg*]-acenapthlen-6-one.



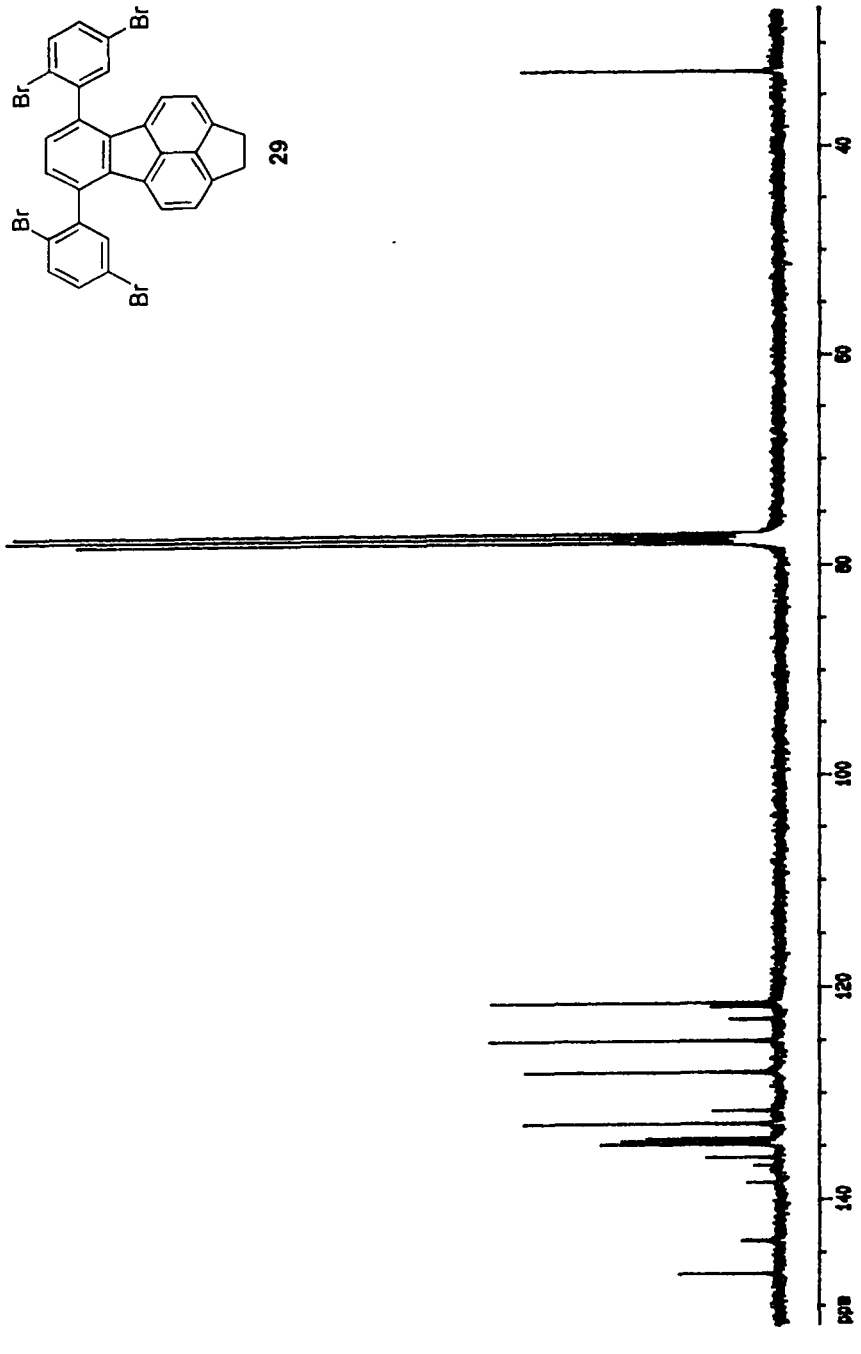
Appendix 33 75.4 MHz ^{13}C NMR Spectrum of 5,7-bis(2,5-dibromobenzo)-1,2-dihydro-6H-dicyclopent[*a,fg*]-acenapthlen-6-one.



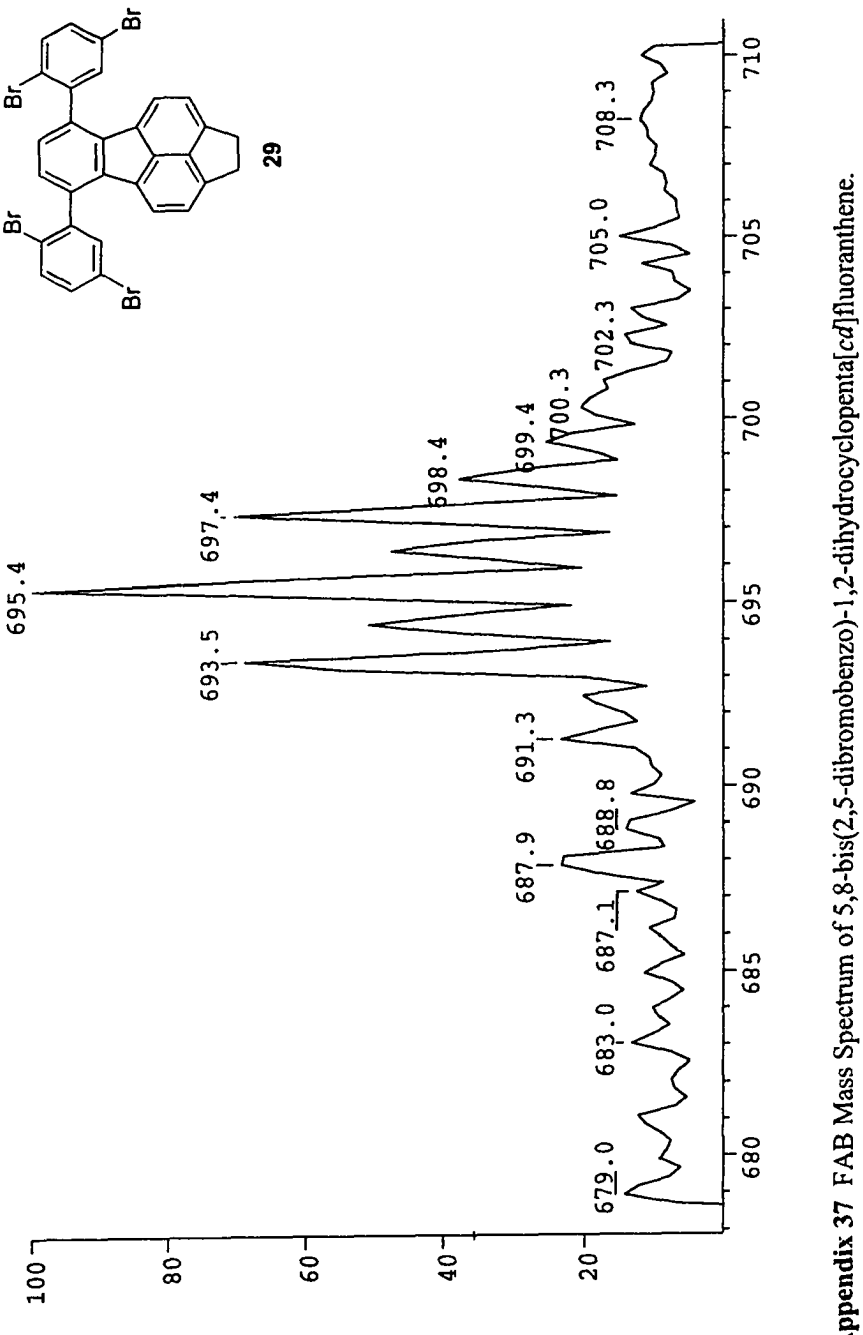
Appendix 34 FAB Mass Spectrum of 5,7-bis(2,5-dibromobenzo)-1,2-dihydro-6H-dicyclopent[*a,fg*]-acenapthlen-6-one.



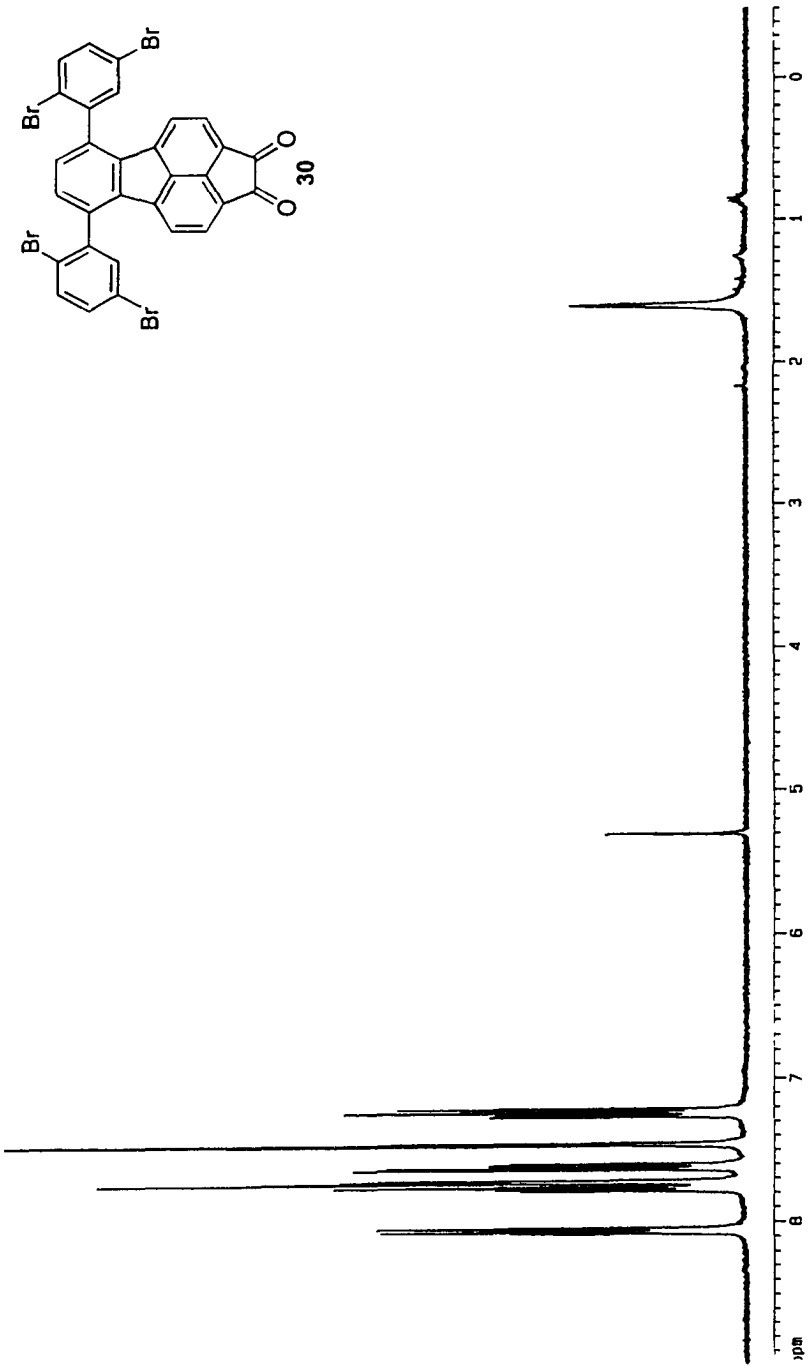
Appendix 35 250 MHz ^{1}H NMR Spectrum of 5,8-bis(2,5-dibromobenzo)-1,2-dihydrocyclopenta[*cd*]fluoranthene.



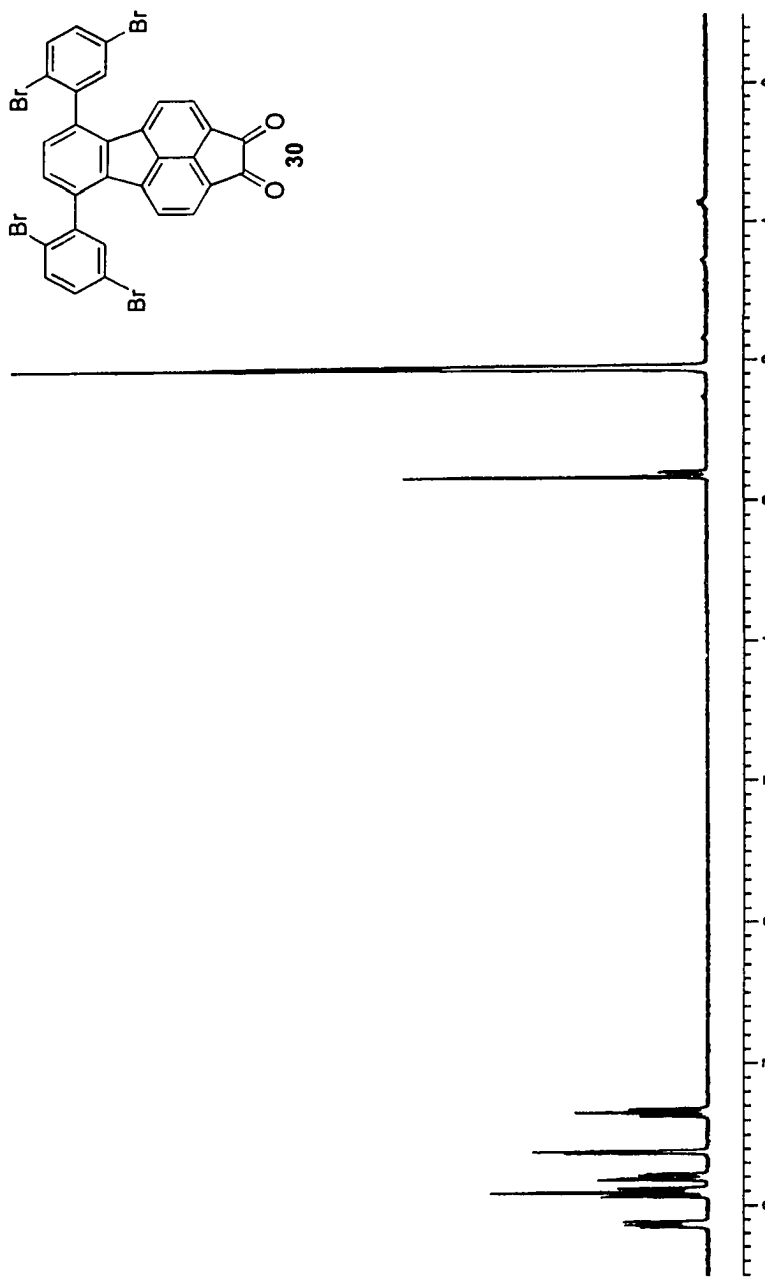
Appendix 36 75.4 MHz ^{13}C NMR Spectrum of 5,8-bis(2,5-dibromobenzo)-1,2-dihydrocyclopenta[*cd*]fluoranthene.



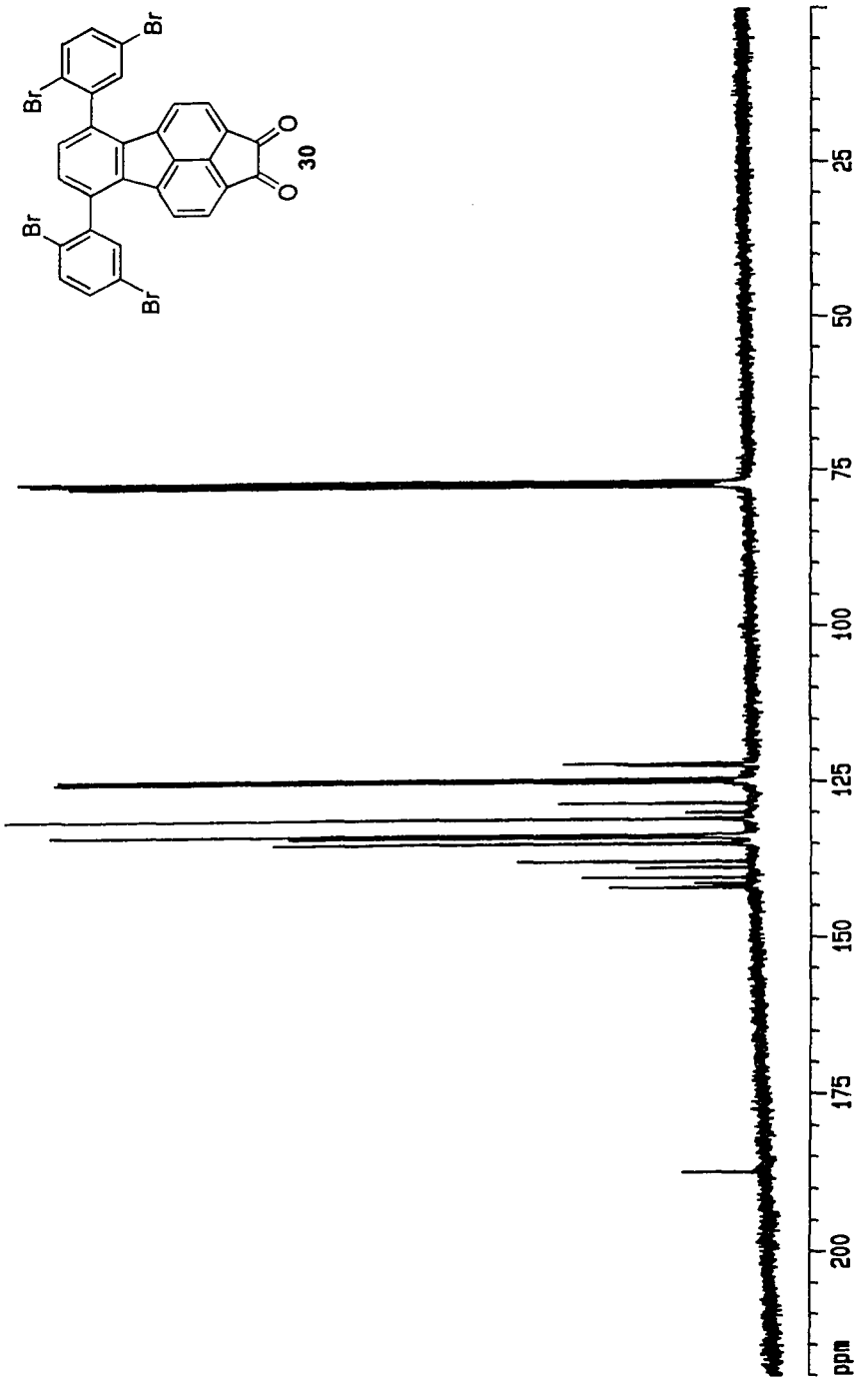
Appendix 37 FAB Mass Spectrum of 5,8-bis(2,5-dibromobenzo)-1,2-dihydrocyclopenta[*cd*]fluoranthene.



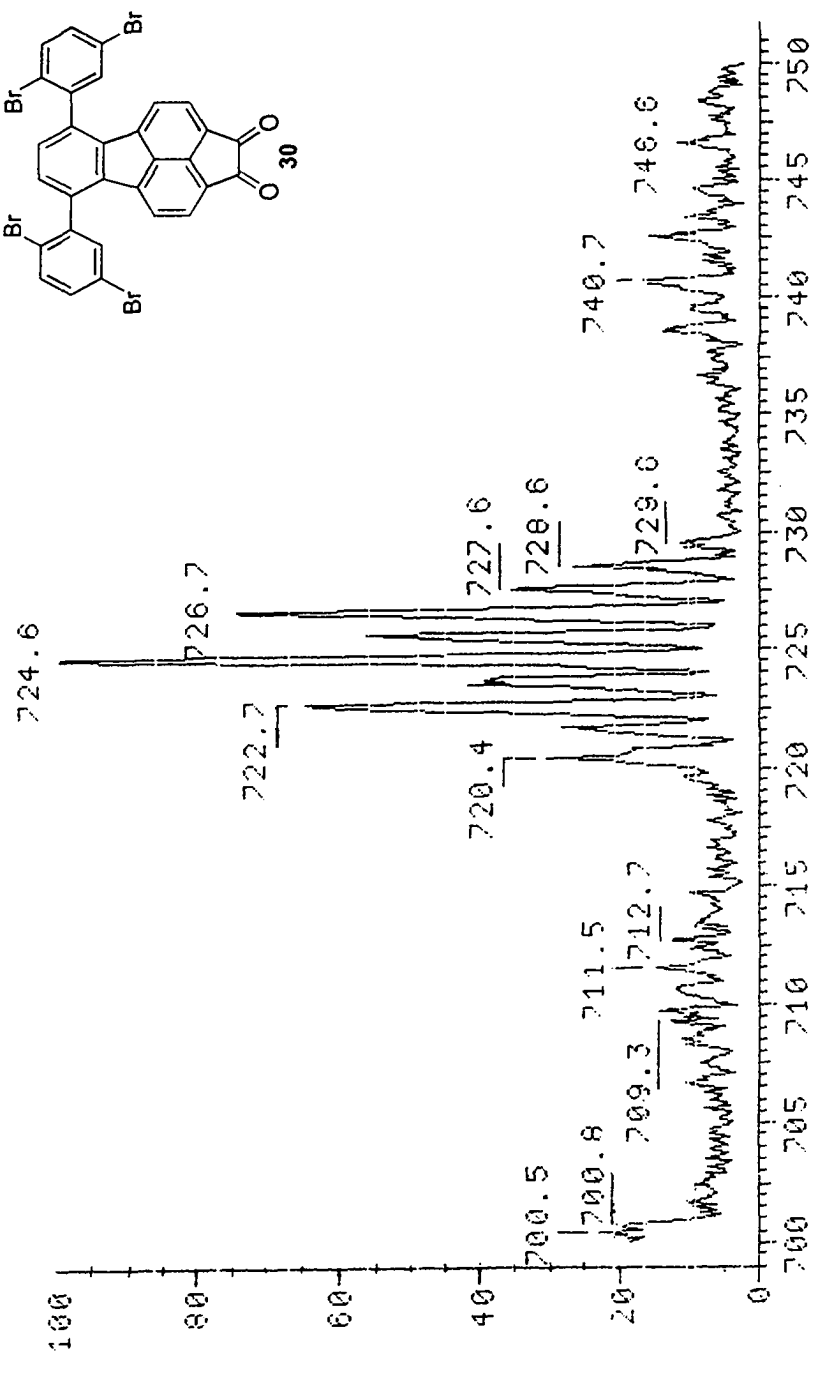
Appendix 38 300 MHz ^{1}H NMR Spectrum of 5,8-bis(2,5-dibromobenzo)-cyclopenta[*cd*]fluoranthene-1,2-dione.



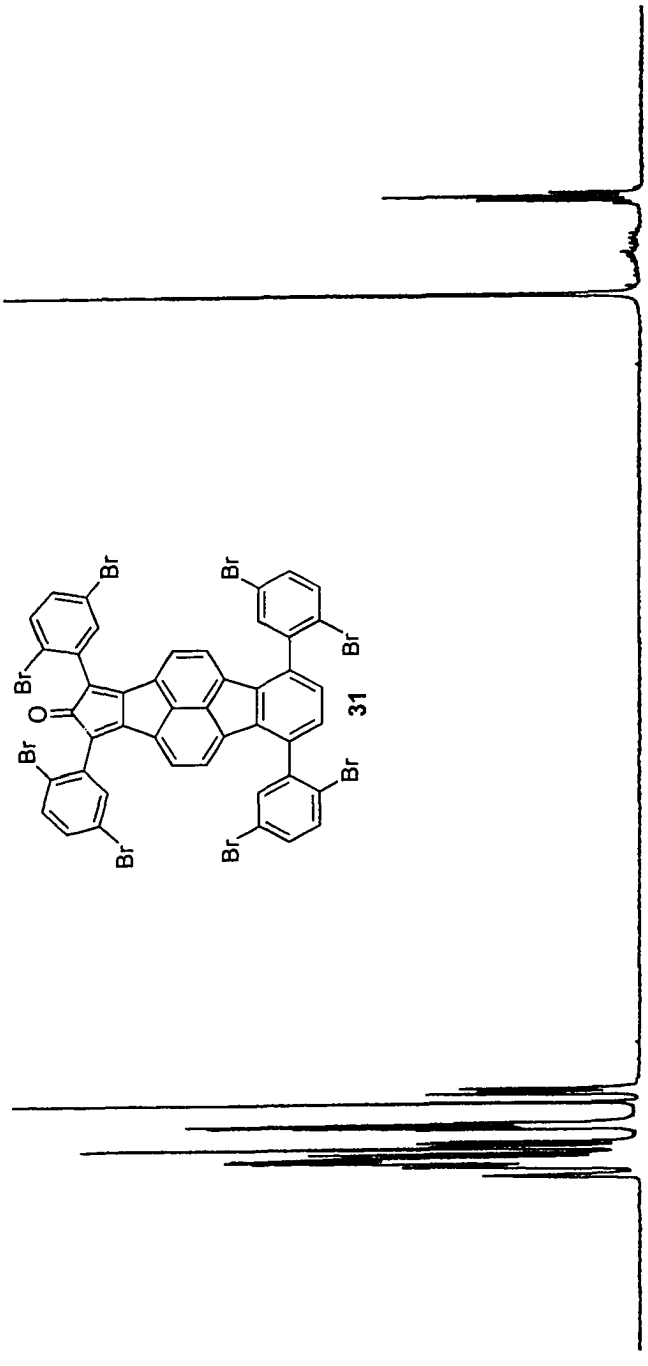
Appendix 39 300 MHz ^{1}H NMR Spectrum of 5,8-bis(2,5-dibromobenzo)-cyclopenta[*cd*]fluornathene-1,2-dione done in DMSO-d_6.



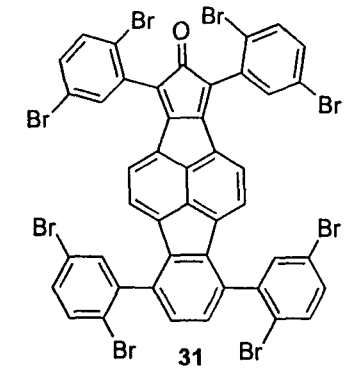
Appendix 40 75.4 MHz ^{13}C NMR Spectrum of 5,8-bis(2,5-dibromobenzo)-cyclopenta[*cd*]fluoranthene-1,2-dione.

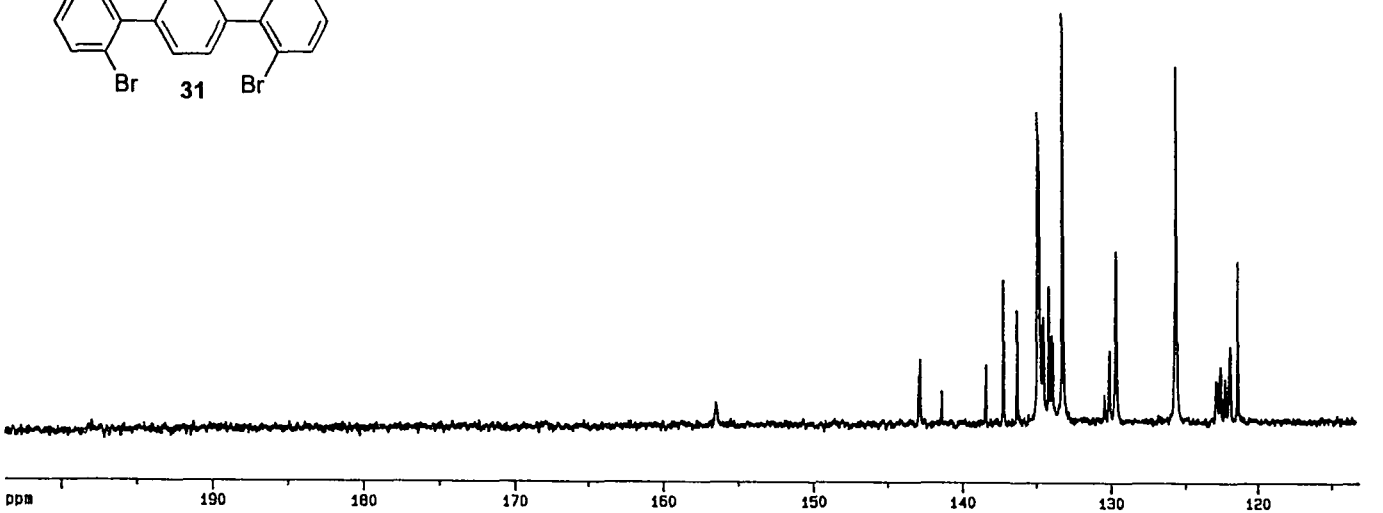


Appendix 41 FAB Mass Spectrum of 5,8-bis(2,5-dibromobenzo)-cyclopenta[*cd*]fluornathene-1,2-dione.

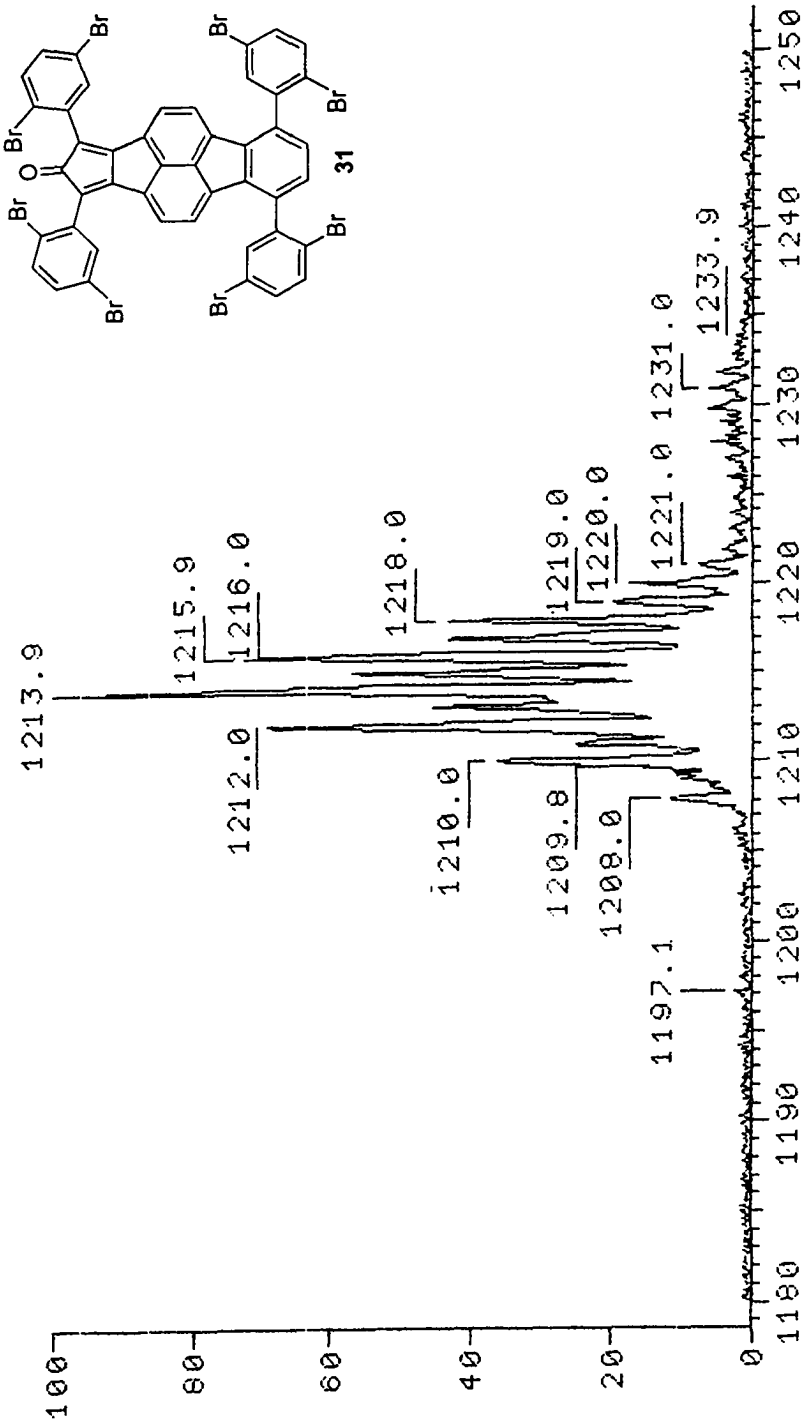


Appendix 42 250 MHz ^{1}H NMR Spectrum of 1,3,6,9-tetrakis(2,5-dibromophenyl)-2*H*-pentaleno[,1,2,3-*cd*]fluoranthene-2-one.

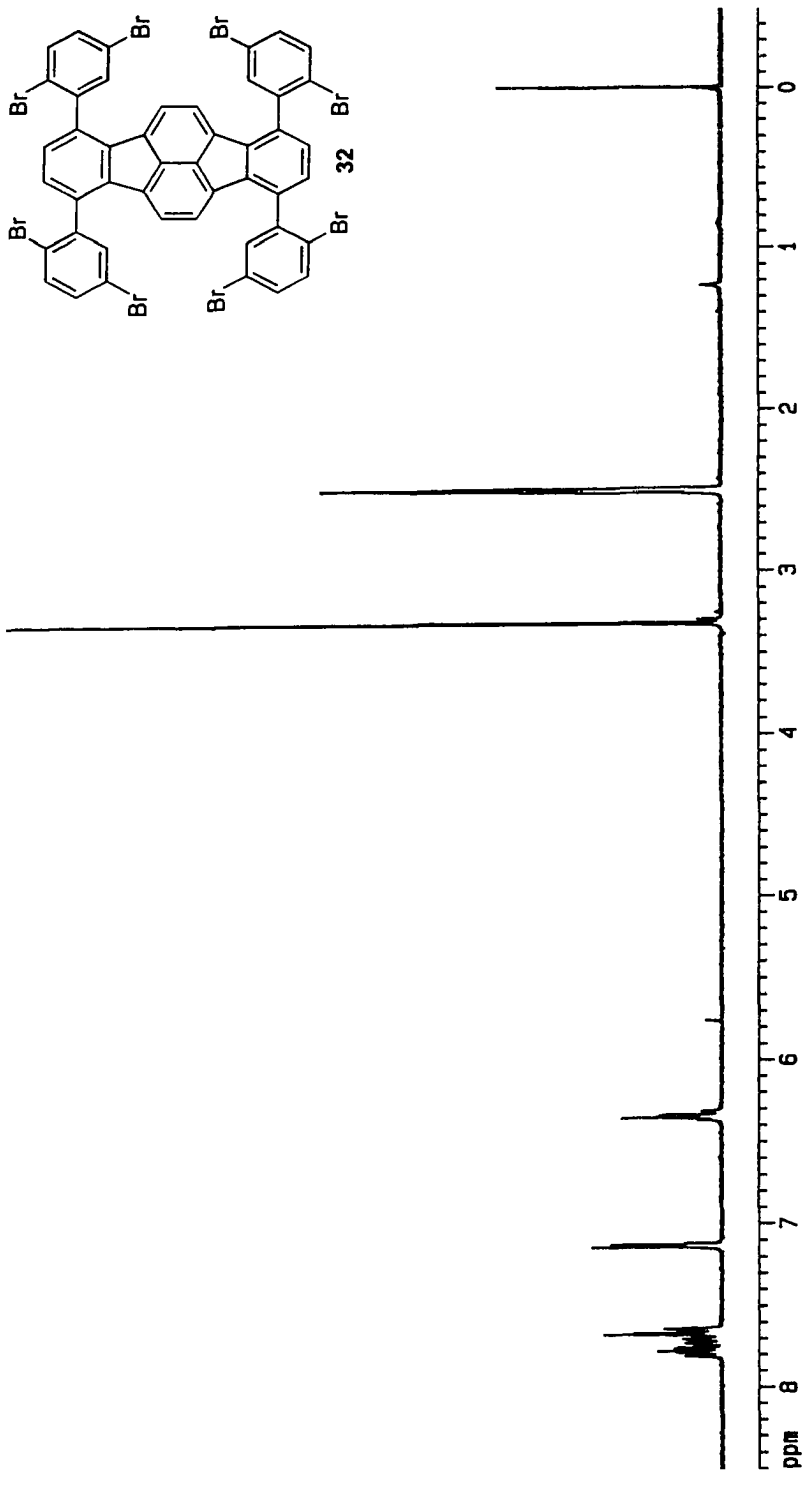




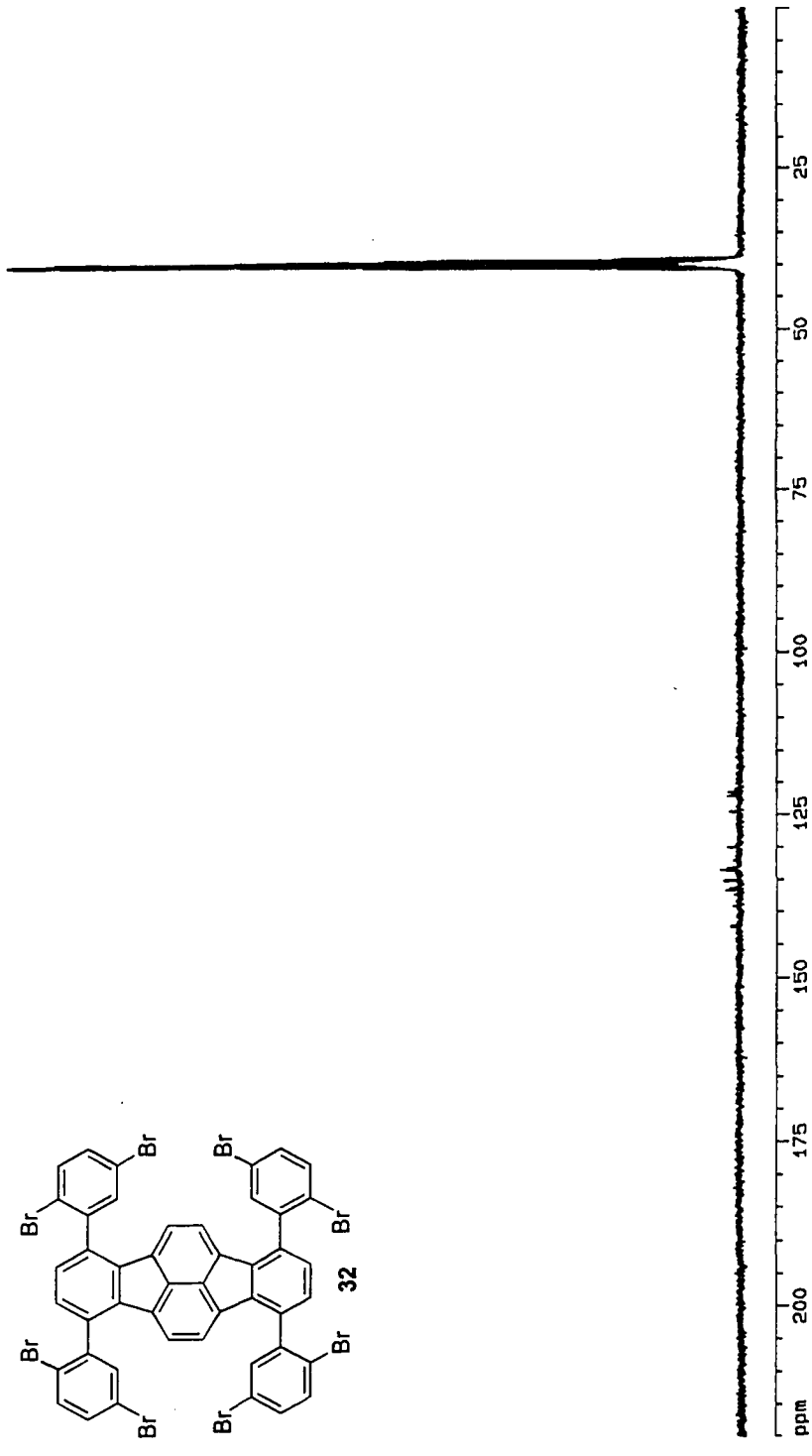
Appendix 43 75.4 MHz ^{13}C NMR Spectrum of 1,3,6,9-tetrakis(2,5-dibromophenyl)-2*H*-pentaleno[,1,2,3-*cd*]fluoranthene-2-one done in $CDCl_3$.



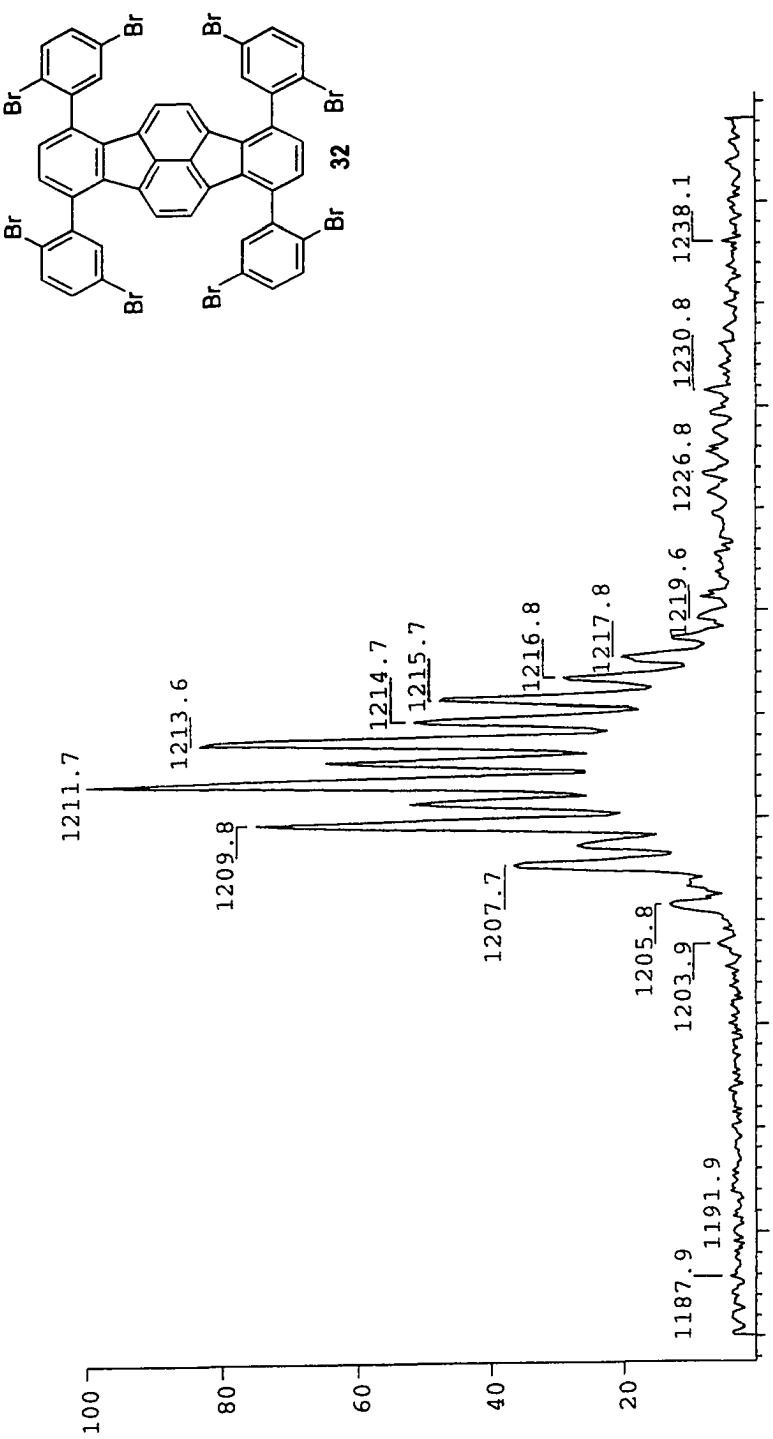
Appendix 44 FAB Mass Spectrum of 1,3,6,9-tetrakis(2,5-dibromophenyl)-2*H*-pentaleno[,1,2,3-*cd*]fluoranthene-2-one.



Appendix 45 300 MHz ^{1}H NMR Spectrum of 1,4,7,10-tetrakis(2,5-dibromophenyl)-indeno[1,2,3-*cd*]fluoranthene done in DMSO-d_6.



Appendix 46 75.4 MHz ^{13}C NMR Spectrum of 1,4,7,10-tetrakis(2,5-dibromophenyl)-indeno[1,2,3-*cd*]fluoranthene done in DMSO-d_6.



Appendix 47 FAB Mass Spectrum of 1,4,7,10-tetrakis(2,5-dibromophenyl)-indeno[1,2,3-*cd*]fluoranthene.

VITA

Mark D. Clayton was born in Cynthiana, Kentucky, on June 28, 1971. He graduated from Pendleton County Memorial High School in June of 1989. He married Kendra K. Wilson on January 1, 1994, and received a bachelor of science degree in Chemistry from the University of Kentucky in May of that same year. In June of 1994 he entered the Graduate Program at Louisiana State University where he began his research under the direction of Dr. Peter Rabideau. He is currently employed at General Electric Appliances in Louisville, Kentucky, and will be awarded the degree of Doctor of Philosophy in December 1998.

DOCTORAL EXAMINATION AND DISSERTATION REPORT

Candidate: Mark D. Clayton

Major Field: Chemistry

Title of Dissertation: Advances in the Chemistry of Fullerene Fragments

Approved:

Major Professor and Chairman

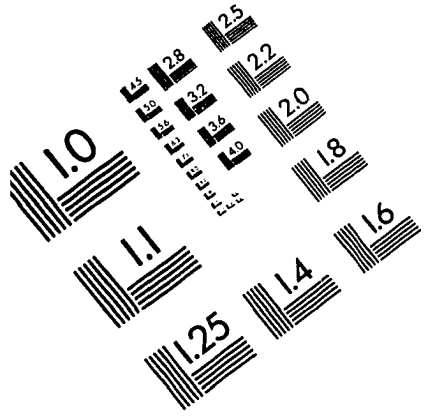
Dean of the Graduate School

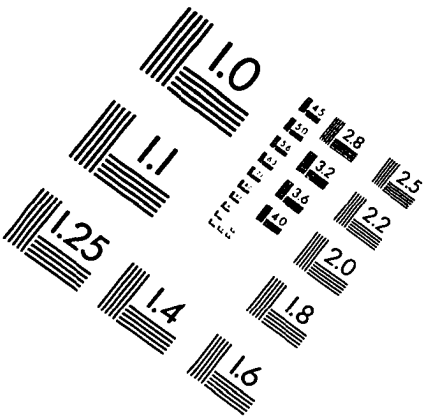
EXAMINING COMMITTEE:

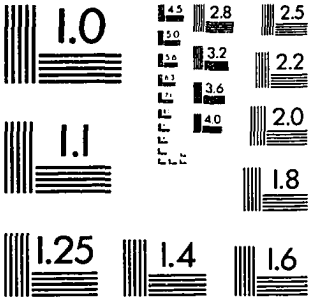
Date of Examination:

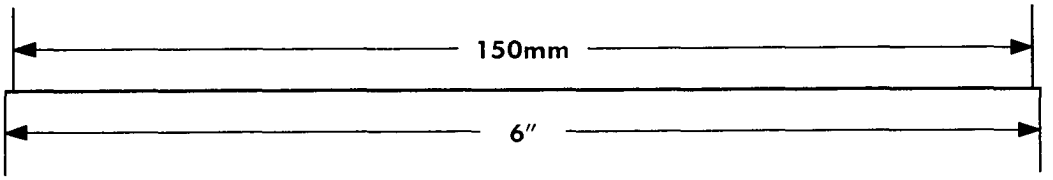
October 23, 1998

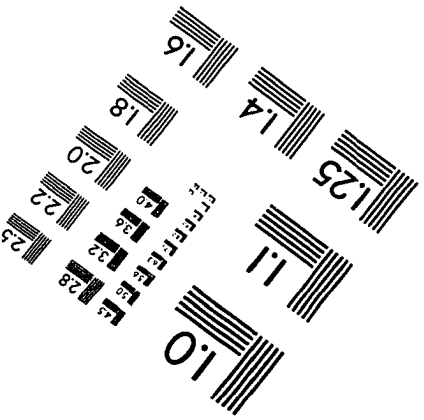
IMAGE EVALUATION
TEST TARGET (QA-3)











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